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<p>(21) International Application Number: PCT/JP87/00401</p> <p>(22) International Filing Date: 18 June 1987 (18.06.87)</p> <p>(31) Priority Application Number: 61/141345</p> <p>(32) Priority Date: 19 June 1986 (19.06.86)</p> <p>(33) Priority Country: JP</p> <p>(71) Applicant (for all designated States except US): ASAHI KASEI KOGYO KABUSHIKI KAISHA [JP/JP]; 2-6, Dojimahama 1-chome, Kita-ku, Osaka-shi, Osaka 530 (JP).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only) : ISHIO, Tadashi [JP/JP]; 3-13-3, Higashiasahigaoka, Suzuka-shi, Mie 510-02 (JP). MATSUMURA, Daisuke [JP/JP]; 1-3, Hiratanakamachi, Suzuka-shi, Mie 513 (JP).</p>		<p>(74) Agents: ASAMURA, Kiyoshi et al.; Room 331, New Ohtemachi Building, 2-1, Ohtemachi 2-chome, Chiyo-da-ku, Tokyo 100 (JP).</p> <p>(81) Designated States: AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, NL (European patent), US.</p> <p>Published With international search report.</p>																								
<p>(54) Title: HEAT SHRINKABLE CYLINDRICAL LAMINATED FILM</p>																										
<p>(57) Abstract</p> <p>A heat shrinkable cylindrical laminated film having a polyvinylidene chloride type resin (I) as an oxygen gas barrier core layer, on the both surface side of which 1 or 2 resin layers are arranged respectively and consisting of 3-5 layers with total, characterized in that the cylindrical exterior surface resin layer on said layer (I) comprises a crosslinked polyolefin type resin layer (II) having a gel fraction [x] at the outermost layer of 25-70 % by weight, a gel fraction [y] at the surface layer in the side of the layer (I) of 40 % by weight or less and a gradient of gel fraction represented by [y/x] of 0.6 or less and the joint of said layers (I) and (II) comprises a laminate of a joint in a state denaturated by electron rays.</p> <div data-bbox="690 1165 1485 2051"> <table border="1"> <caption>Estimated data points from the graph</caption> <thead> <tr> <th>Penetrating Depth μ</th> <th>Dose, % (BROKEN LINE 1)</th> <th>Dose, % (BROKEN LINE 2)</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>100</td> <td>100</td> </tr> <tr> <td>100</td> <td>105</td> <td>95</td> </tr> <tr> <td>200</td> <td>115</td> <td>70</td> </tr> <tr> <td>300</td> <td>120</td> <td>30</td> </tr> <tr> <td>400</td> <td>115</td> <td>0</td> </tr> <tr> <td>500</td> <td>110</td> <td>-</td> </tr> <tr> <td>600</td> <td>105</td> <td>-</td> </tr> </tbody> </table> </div>			Penetrating Depth μ	Dose, % (BROKEN LINE 1)	Dose, % (BROKEN LINE 2)	0	100	100	100	105	95	200	115	70	300	120	30	400	115	0	500	110	-	600	105	-
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500	110	-																								
600	105	-																								

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DESCRIPTION

A HEAT SHRINKABLE CYLINDRICAL LAMINATED FILM

1 TECHNICAL FIELD

This invention relates to an improvement of cylindrical laminated films which are used for heat shrinking packages of irregularly shaped fatty food as contents such as raw meat, processed meat or the like.

BACKGROUND ART

Heat shrinkable cylindrically laminated films comprising 3 - 5 layers, one of which is a polyvinylidene chloride type resin (hereinafter referred to as PVDC) as an oxygen gas barrier layer and having a total thickness of 40 - 80 μ are well known in the art. Typical laminated films which are currently commercially available include, for example, a laminated cylindrical film comprising 3 layers of an ethylene-vinyl acetate copolymer resin (hereinafter referred to as EVA) at the exterior side of the cylinder/a PVDC/a cross-linked EVA at the interior side of the cylinder according to Japanese Patent Application Publication No. 43024/83 (US Patent No. 3,741,253); a laminated cylindrical film comprising 3 - 5 layers of a specific polyolefin resin blend at the exterior side of the cylinder/a PVDC/a specific polyolefin resin blend at the interior side of the cylinder according to Japanese Patent Application Publication

- 1 No. 40988/85 (US Patent No. 4,390,587); and a laminated
cylindrical film comprising 4 - 5 layers of an EVA/a
PVDC/an ionomer resin at the interior side of the
cylinder according to Japanese Patent Application
5 Publication No. 2192/80 (US Patent No. 4,161,562).
These laminated cylindrical film have occupied the market
share as the packaging materials used for packaging in
tight irregularly shaped fatty foods as contents by heat
shrinking by proposing as the sales point their unique
10 advantages such as excellent appearance owing to their
transparency, their heat shrinkability at low tempera-
ture which will not damage the freshness of contents,
excellent handling and working properties and the like.

However, with the proceeding of the improvement
15 of packaging efficiency by the introduction of high speed
packaging technique using a rotary chamber vacuum packaging
machine, new problems of quality have happened in the
packaging field, which problems are those of quality of
design and cannot be solved with the aforementioned packag-
20 ing materials.

In other words, as the result of research of
the present inventors, the applicability of the high
speed packaging technique may be decided by the following
three points; first of all, possibility of making a
25 certain sealed part having oil resistance while shorten-
ing the time required for tight sealing of packing bags
filled with contents under reduced pressure; secondly,
securing the cruel treatment resistance of the films so
as to resisting rough handling of packaged articles

1 accompanied with the increase of packaging speed under
severe conditions; and third, enhancement of oil
resistance of interior and exterior layers, in
particular, on the treatment at high temperature. In
5 addition, these new quality requirements must be
satisfied without damaging the conventional quality level
and is also in a high level.

Specifically, referring to the cruel treatment
resistance as an index of causing no failures such as pin
10 hole or break of bag on handling of a package, require-
ment level has been raised and a commercially available
film comprising EVA/PVDC/crosslinked EVA which has been
evaluated to have a toughness to ensure that the film can
be used for direct packaging of meat with sharp bone at
15 the initial application (see the effect of Japanese
Patent Application Publication No. 43024/83) is now
evaluated in the new market requirements to be insuf-
ficient in toughness owing to high incidence of failures
such as pin hole or break of a sealed part during handl-
20 ing the film even if the content is changed to meat
without bone so that sharp extrusion will not be detected
in it on touching with hand.

However, these films are not easily modified or
improved. The reason depends on that a PVDC layer as a
25 core layer will be yellowed or deteriorated upon
irradiation of electron rays and thus it is difficult to
carry out crosslinking in a state of a laminate, which
makes it impossible to employ coextrusion technique

1 excellent in interlaminar strength. Furthermore, it is
very difficult to form a cylindrical coextrusion laminate
using the PVDC layer and finally to make a laminated film
the exterior surface side of which is crosslinked. There
5 has also been proposed a non-crosslinked resin obtained
by the examination of resin species to be used and its
laminate construction, but the counterproposal is
inferior in effect to that of using a crosslinked layer
which improves both film forming property by drawing and
10 film property itself. Accordingly, a laminated film
containing as a modifying layer a polyolefin type resin
layer having a sufficient degree of crosslinking must be
prepared by the method such as described in Fig. 1 of US
Patent No. 3,741,253, in which a cylindrical EVA layer is
15 extruded and crosslinked with radiation, a PVDC layer and
an EVA layer are cylindrically extruded sequentially on
the EVA layer, and these layers are melt-extruded from a
coating die in the outside of the die to form a directly
adhered laminate each other, which is drawn by an
20 inflation method to form a cylindrical laminated film.
This method has disadvantages that it is not economical
as it requires technique of a high order and that the
crosslinked layer of the film obtained will be an inner-
most layer of the cylindrical film.

25 As disclosed in Japanese Patent Application
Kokai (Laid-Open) No. 23752/87 (by virtue of a right of
priority based on US Patent Application No. 735,082/85),
the method of irradiating electron rays over the whole

1 layers of a laminated film which has been prepared by
coextrusion and drawing may be appreciated in the point
that an effect of crosslinking-drawing is abandoned and
both the modifying effect of crosslinking on the
5 polyolefin type resin and the improving effect on the
bonding between the polyolefin type resin and the PVDC
layer are utilized. But the method has disadvantages
that the PVDC layer is inevitably deteriorated by the
irradiation of electron rays (lowering of oxygen gas
10 barrier properties) and that the effect of crosslinking-
drawing to be abandoned is very large. Further, it has
been confirmed that in the laminated film obtained by
irradiating the whole layers typified by the films
disclosed in Japanese Patent Application Kokai (Laid-
15 Open) No. 143086/76 (US Patent No. 4,044,187) and US
Patent No. 3,821,182 the PVDC layer is deteriorated
drastically (see Tables 4 and 5).

DISCLOSURE OF INVENTION

The object of this invention from this view-
20 point is to provide a cylindrical laminated film which
satisfies the aforementioned new required quality, that
is to say, the film in which most of the evaluation items
listed in Table 11 is maintained in high levels,
characterized in that the yellowing or deterioration of
25 the core layer of a cylindrical laminated film which has
a PVDC layer as the core layer and is obtained by
coextrusion is minimized to form a laminated film in

1 which the exterior side of the cylinder is modified by
crosslinking and the layer construction is adjusted to
the optimal. In other words, the object of this inven-
tion is to provide a heat shrinkable cylindrical
5 laminated film having a polyvinylidene chloride type
resin (I) as a gas-impermeable (i.e. oxygen barrier) core
layer, on the both surface sides of which 1 or 2 resin
layers are arranged respectively and consisting of 3 - 5
layers with total, characterized in that the cylindrical
10 exterior surface resin layer on said layer (I) comprises
a crosslinked polyolefin type resin layer (II) having a
gel fraction [x] at the outermost layer of 25 - 70% by
weight, a gel fraction [y] at the surface layer in the
side of the layer (I) of 40% by weight or less and a
15 gradient of gel fraction represented by $[y/x]$ of 0.6 or
less and the joint of said layers (I) and (II) comprises
a laminate of a joint in a state denaturated by electron
rays.

BRIEF EXPLANATION OF THE DRAWINGS

20 Figs. 1, 2, 3-A, 3-B and 4 are respectively
graphs illustrating the experimental results referring to
doses of electron rays; Fig. 5 is a schematic chart
illustrating a manufacturing process of the film of this
invention;

25 Figs. 6, 8 and 9 are respectively graphs
illustrating the experimental results referring to the
effects of irradiation of electron rays; and

1 Fig. 7 is an analytical diagram illustrating
the components of the sealable resin layer in the film of
this invention.

/

BEST MODE FOR CARRYING OUT THE INVENTION

5 This invention is now described in detail
referring to the drawings and the tables. First of all,
this invention is explained from the aspect of the
process for preparing the laminated film of this inven-
tion as a new laminated film, whereby the source of its
10 novelty will be understood more readily.

The process for preparing the laminated film of
this invention typically includes the crosslinking-
drawing method by (i) forming a cylindrical laminate by a
coextrusion method, (ii) irradiating electron rays for
15 the exterior surface of the cylindrical laminate, and
then (iii) drawing the irradiated laminate to utilize the
crosslinking-drawing effect. The process is character-
ized in that the electron rays are irradiated into the
layer (II) at the exterior surface side of the cylinder
20 so as to afford crosslinking (gel fraction) gradient and
thus to subject sufficient crosslinking to the layer
(II), while denaturation by electron rays is caused also
at the joint area of the layer (II) and the core layer
(I) but the radiation has been attenuated to give a small
25 exposed dose to the core layer (I).

The reason is illustrated in Fig. 9 (corre-
sponding to Experimental Example 1) and in Fig. 8 (corre-

1 sponding to Experimental Example 7). That is to say,
Fig. 9 is a conceptional curves illustrating the relation-
ship between the exposed dose of electron rays to the
film and the (positive or negative) effect afforded by
5 the irradiation (crosslinking), in which the axis of
abscissa represents the exposed dose (Mrad) at the
surface of the film and the axis of ordinate represents
the non-defective ratio of the film group. In these
curves, plotting by the triangle mark Δ indicates the
10 factor which illustrates the degree of deterioration of
the PVDC layer and is represented by the level of non-
defective barrier ratio of the film group upon repeated
flexing with twisting, and the plotting by the circle
mark \circ indicates the factor which illustrates the degree
15 of toughness of the crosslinked-drawn film and is
represented by the level of non-defective ratio of the
film having a high temperature resistance on sealing of
the film. The empty marks indicate the case carried out
according to the process of this invention and the black-
20 painted marks indicate the case carried out according to
a conventional process (total layer irradiation).

From the result illustrated in Fig. 9, it can
be understood that in the conventional (blank-painted)
process the crosslinking effect rapidly increases from
25 about 4 Mrad and reaches the maximum level at about 6
Mrad, but the deterioration of PVDC increases markedly
from about 2 Mrad and the half of the PVDC will exhibit
defectiveness in oxygen gas barrier property even at an

1 exposed dose of about 3 Mrad in which the aforementioned
crosslinking effect does not appear, so that it is
impossible to select any appropriate range of exposed
dose in which irradiation (crosslinking) effect can be
5 taken without the deterioration of the PVDC layer.

On the other hand, Fig. 9 indicates that
according to the process of this invention (plotting with
empty marks), development of the crosslinking effect
remains at a low level and exposed dose of about 7 - 10
10 Mrad is required for obtaining the crosslinking effect at
a maximum level, but the deterioration of the PVDC at the
same dose level is also reduced remarkably, so that it is
possible to select an appropriate range of exposed dose
for remaining the deterioration of the PVDC layer at a
15 minimum level while maintaining the crosslinking effect
at a high level.

Fig. 8 is a graph obtained from experiments for
illustrating the improvement of adhesion strength between
the core layer and the adjacent layers to the exposed
20 dose. Plotting by empty circles O represents the result
obtained by the process of this invention and plotting by
black-painted circles ● represents the result obtained by
the conventional process (i.e. the process for adhering
the adjacent layers immediately after irradiation).

25 To be noted amongst the results of Fig. 8 is
the phenomenon of increasing the difference of effects
between both curves accompanied with the increase of the
exposed dose. In other words, even if the difference of

1 the adhesion strength inherently present between both
curves (as compared with each other at the exposed dose
of 0 Mrad) be the one generated by the difference of the
melt-extruded coating method (a layer is melt-extruded
5 from a coating die onto a tube and directly adhered to a
tube in the outside of a die; hereinafter referred to as
melt-extruded coating method) and the co-extrusion method
as is generally recognized, it can be considered that the
increase of the adhesion strength at the neighborhood of
10 the exposed dose of 7 - 10 Mrad is one of the great
effects brought about by the process of this invention
which makes it possible to apply the exposed dose of 7 -
10 Mrad without the deterioration of the PVDC layer. The
improvement of adhesion strength between layers is
15 presumably attributed to the crosslinking generated
between layers in some degree. Accordingly, probability
of the crosslinking reaction will be increased in propor-
tion to the exposed dose passing through the interface of
the layers. Therefore, if the irradiation of electron
20 rays onto the layers which have been tightly bonded to
each other and the adhesion of layers after the irradi-
ation are compared, the probability of crosslinking
between the adhesion part will be apparently larger in
the former than in the latter. The difference of the two
25 curves in Fig. 8 should be noted as an index of the
aforementioned phenomenon.

The phenomena illustrated in Figs. 8 and 9 is
the ones which have successfully been utilized for the

1 first time by the process of this invention. Therefore,
the laminated film prepared according to the process of
this invention is a cylindrical laminated film having a
variety of properties that the exterior layer side of the
5 cylindrical laminated film is first of all modified by
crosslinking and the degree of the crosslinking (exposed
dose) is sufficient to carry out the modification by
crosslinking-drawing of not only the exterior layer
itself but also the other layers which will be modified
10 together with drawing of the exterior layer, while most
part of the PVDC layer as the core layer is not deterio-
rated to ensure that the oxygen gas barrier property
after flexing with twisting is maintained and the PVDC
layer and the exterior layer are bonded satisfactorily.
15 Figs. 8 and 9 also illustrate the aforementioned facts.

Next, this invention will be explained refer-
ring to the prevention of the deterioration of the PVDC
layer as the core layer in spite of the irradiation of
electron rays onto the exterior layer of the cylindrical
20 laminated film of this invention.

Fig. 1 (corresponding to Experimental Example
2) is an experimental graphs of dosage distribution of an
electron rays irradiation apparatus, and the axis of
ordinate represents dose (%) and the axis of abscissa
25 represents the penetrating depth of electron rays (μ).
The solid line represents the result with the apparatus
used in this invention, the broken line 1 represents the
result with a conventional scanning electron rays

1 irradiation apparatus having an acceleration voltage of a high voltage and the broken line 2 represents the result by adjusting the broken line 1 to a maximum.

As apparent from Fig. 1, the irradiation
5 apparatus used in this invention is modified in many points of irradiation method, titanium foil, its cooling method and the like to ensure that electron rays will not penetrate a deep point of the film.

Fig. 2 (corresponding to Experimental Example
10 2) represents a schematic diagram for illustrating the application method of dosage distribution of the solid line in Fig. 1, in which the axis of ordinate represents the exposed dose of electron rays (Mrad) and the axis of abscissa represents the enlarged thickness in a sectional
15 direction of a film. That is, the figure represents structural conception of the zone A as the surface layer of a polyolefin type resin layer (II), the zone B as the PVDC layer (I) and the zone C as a part of the adhesive shrinkable resin layer (III), respectively. Seven curves
20 (a), (m), (b), (c), (d), (e) and (f) in Fig. 2 represent the results obtained by the irradiation of electron rays having a variety of dosage distribution in relation with the aforementioned film thickness. The curves (m), (b) and (c) illustrate the results obtained by using the film
25 of this invention, and the curves (a), (d), (e) and (f) illustrate the results obtained by using a referential article. In other words, the dosage distribution in the film of this invention may be illustrated by the curves

1 which are attenuated obliquely within the surface layer
and the terminal parts of the curves pass across the
adhesion part of the surface layer and the core layer and
penetrate the PVDC layer. However, in the case illust-
5 rated in Fig. 2, the terminal parts presumably remain in
substantially central part of the PVDC layer and will not
reach the adhesive shrinkable resin layer. Accordingly,
it can be considered that the dosage accepted by the
surface layer of the laminated film of this invention is
10 sufficient to improve the drawing sate of the polyolefin
type resin and also sufficient even at its adhesion part
with the PVDC layer to improve the adhesion strength of
the two layers, while the PVDC layer will accept the
dosage as low as one third of that in the surface layer
15 and thus the deterioration of the PVDC layer is
controlled to the minimum.

This is to say, this invention is accomplished
by conducting researches about the relationship of the
dosage level and the distribution profile of the dosage
20 in the direction of the thickness so as to satisfy the
required quality of the film from the standpoint of
advantages and disadvantages of the polyolefin type resin
layer and the PVDC layer.

Figs. 3-A and 3-B (corresponding to Experi-
25 mental Example 4) are experimental diagrams illustrated
in the same manner as in Fig. 2. In these figures,
dosage distribution of a crosslinked film by the irradi-
ation of electron rays which film has hitherto been

1 proposed as the prior invention, in which the films
obtained in the case of dosages of (g) - (j) are compara-
tive products corresponding to those of this invention.
In addition, the results of evaluation of the films
5 illustrated in Figs. 2, 3-A and 3-B are listed in Tables
2 and 5 to confirm the excellent properties of the film
of this invention.

Fig. 4 (corresponding to Experimental Example
5) is a schematic diagram illustrating this invention
10 which is created to adjust the contradictory requirements
that the deterioration of film formability accompanied
with excessive crosslinking should be avoided and that
the degree of crosslinking of the whole layers should be
maintained in a high level, in which the axis of abscissa
15 represents thickness of the film and the axis of ordinate
is the degree of crosslinking (gel fraction).

Fig. 4 illustrates the effect of a crosslinked
polyolefin type resin layer which comprises the lamina-
tion of two polyolefin type resins having different
20 crosslinking efficiencies, one of which resins having a
lower crosslinking efficiency is used as an exterior
surface.

In this case, the broken line illustrated in
the left upper part of the figure represents the
25 crosslinking profile of the polyolefin type resin layer
comprising only one resin layer having a moderate
crosslinking efficiency, which profile exceeds the
limitation for easy film formation by drawing (partial

1 gel fraction of 70% by weight) and enters into the region
of defective film formation. But if an outermost layer
having a lower crosslinking efficiency (i.e., having a
lower gel fraction at the same dosage as above) is
5 further laminated on the polyolefin type resin, the
crosslinking profile does not enter into the region of
defective film formation as is illustrated by the solid
line. In this case of the crosslinking profile illust-
rated by solid line an internal surface layer having a
10 higher crosslinking efficiency (i.e., having a higher gel
fraction at the same dosage as above) is further arranged
to ensure that the whole degree of crosslinking of the
crosslinked polyolefin type resin layer will be substan-
tially in the same level as of the resin layer having a
15 moderate degree of crosslinking.

The laminated film of this invention is a novel
film which has been accomplished on the basis of inform-
ation of the irradiation method of electron rays and the
layer construction which are illustrated in Figs. 1 -4
20 and Tables 1 and 2.

The usefulness of the film will be explained
with reference to the features of the production process
of the film of this invention and the films of this
invention prepared according to the features, that is,
25 the scope of claims of this invention.

Fig. 5 is a schematic diagram of production
process of the film of this invention.

Referring to the production example of the film

1 of this invention, respective layer constructing resins
having been molten in three or four extruders 1, 2 and 3
(and/or 3') are introduced into a circular die 4 to form
a laminate and coextruded as a laminated cylindrical
5 parison 5. The cylindrical product 5 is rapidly cooled
sufficiently with a cooling apparatus 6, folded into a
plain plate with pinch rolls 7 and introduced into
electron beam irradiation chamber 8. Numerical marks 9,
9' and 9" represent a group of guide rolls.

10 Within the irradiation apparatus 8 protected
with lead plates 10 or the like, the surface side of said
parison plate 13 is directly irradiated with electron
rays generated from the electron beam irradiation
apparatus 11 through a titanium foil 12. The parison 13
15 is turned around with a turning roll 14 so that the
traveling position will be changed on going and coming
and both the surface and back of the parison will be
continuously crosslinked by irradiation of electron rays.

 The crosslinked parison 15 is introduced into a
20 heating bath 17 by the group of guide rolls 16 - 16'",
heated to a temperature of about 60 - 98°C with a heat
transfer medium 18, subjected to inflation biaxial
orientation accompanied with cooling with a air blast
cooling ring 22 at a position between a group of pinch
25 rolls 19 and 20, flexed into a flat film by a deflator 21
and batched on as a flat cylindrical film 24 to a rolling
axis 23.

 During a series of this production process, it

1 is basically distinguished from the conventional process
(e.g., a process disclosed in US Patent No. 3,741,253)
that the laminated cylindrical product having the PVDC
layer as a core layer and formed by co-extrusion is
5 directly irradiated with electron rays from not the
interior but the exterior surface of the cylinder to
obtain a cylindrical laminated film, the exterior surface
of which has been crosslinked.

Accordingly, it is a main claim that the
10 subject matter of this invention is intended to express
the process of denaturation by crosslinking which is
distinguished from the conventional technique in the
points that in the form of a laminated film without
having been crosslinked prior to lamination effect of
15 modification by crosslinking (denaturation) is utilized,
while the deterioration of the PVDC layer is reduced to
the minimum, by the degree of denaturation by crosslink-
ing (gel fraction) [y] at the surface layer part of the
crosslinked polyolefin type layer (II) in the core layer
20 (I) side, the degree of the denaturation by crosslinking
(gel fraction) [x] at the exterior surface layer part of
the same resin layer and the gradient of the gel fraction
[y/x]. The aforementioned relationship is listed in
Table 2 corresponding to Experimental Example 2 and in
25 Table 14 corresponding to Experimental Example 5.

However, as a general principle, said [y] having a value
exceeding 40% by weight is excluded from the object of
the experiment in this invention. The reason is that

1 even if the gradient of the gel fraction $[y/x]$ may be
changed, the PVDC layer of the core layer is deteriorated
too much to match the object of this invention. Such a
phenomenon can be inferred, for example, from respective
5 curves in Fig. 2. Accordingly, said $[y]$ should be a
little value of 40% by weight or less, but it does not
include the gel fraction of less than 0.5% by weight and
having substantially no difference with that of un-
crosslinked article. In order to increase adhesion force
10 between the surfaces of said layer (II) and the (I), it
is important to carry out denaturation by electron rays
(which will be recognized, for example, by the improve-
ment of adhesive strength) while maintaining the surfaces
in contact in tight to each other, and thus said $[y]$ will
15 not be 0.5% by weight or less.

As apparent from Tables 2 and 14 under such
conditions, if the value of $[x]$ exceeds 70% by weight,
film formability by drawing is damaged. If the value is
less than 25% by weight, heat resistance of the film is
20 not satisfactory. In addition, even if $[y]$ is 40% by
weight or less and $[x]$ is in the range of 70 - 25% by
weight, the PVDC layer will be extensively denaturated on
the gradient represented by $[y/x]$ being larger than 0.6.
From the results of No. 141 in Table 14, practical
25 availability of the film on the gradient of 0.6 is
proved.

When the crosslinked polyolefin type resin
layer (II) has an average gel fraction in the range of 20

- 1 - 60% by weight and a ratio of layer thickness in the proportion of 25 - 65% to the total film thickness, preferred degree of crosslinking for exhibiting the crosslinking effect is typified by the results listed in Table 6-A (corresponding to Example, Comparative Example 1).

That is to say, as the advantage of crosslinking of the polyolefin type resin layer (II), first of all, drawing ability of itself is improved and then properties relating to toughness such as heat resistance, oil resistance, falling bag resistance at lower temperature and the like will be improved. The enhancement of the drawing ability controls the film formability of the whole laminated film. Thus, the sealing resin layer (IV) and the PVDC layer (II) which will not be uniformly drawn with ease are oriented in high degree and uniformly, and high heat shrinkability and mechanical properties are given to the whole laminated film.

The relationship of sample Nos. 1 - 9 in Table 6-A indicates that in order to improve the properties mentioned above the average gel fraction is preferably in the range of 20 - 60% by weight and the ratio of the thickness as a layer is preferably in a proportion of 25 - 65% of the total thickness of the film.

In this case, electron rays directly irradiated from the surface side of the laminated film often makes the exterior surface layer of the crosslinked polyolefin type resin layer (II) in an excessive gel fraction to

1 damage the film formability by drawing. It is not easy
to increase only the film formability by drawing without
decreasing the gel fraction of the whole layer (II). As
a countermeasure against the problem, there is proposed a
5 method utilizing a phenomenon illustrated in Fig. 4, in
which the aforementioned layer (II) has a double layer
structure constructed from two resin layers, the
crosslinking efficiencies of which are different from
each other, and one of the resin layers having an lower
10 crosslinking efficiency is arranged as the outermost
layer.

As another embodiment, the cylindrical film of
this invention is a film having excellent interior
sealability and high heat shrinkability. Thus, a useful
15 layer construction in the cylindrical interior side is
required. The adhesive shrinkable resin layer (III) has
a role for adhering the sealing resin layer (IV) and the
core layer (I) in tight and for controlling the heat
shrinkability of the whole laminated film, particularly
20 heat shrinkability at low temperature in cooperation with
the crosslinked layer at the surface side. EVA is
generally used in order to carry out the role. It is
preferred to use an EVA having a vinyl acetate content in
the range of 13 - 20% by weight as the adhesive shrink-
25 able resin layer (III), which is apparent from the
relationship between the vinyl acetate content and
adhesion strength as illustrated with the curve plotted
with empty circles O in Fig. 6.

1 A further embodiment is the employment of a
preferred resin species as the surface layer of the
aforementioned sealing resin layer (IV). This selection
of the species will lead to another remarkable effect
5 exhibited by the film of this invention, and thus the
selection of the resin species therefore is explained in
detail below.

The remarkable effect exhibited by the film of
this invention is an effect for improving the sealing
10 performance which is exhibited by the combination of a
surface crosslinking resin layer and a sealing resin
layer. Specifically, it is a combination of two main
effects of the effect for satisfying the requirements for
reducing the time needed to accomplish sealing and
15 improving packaging ability and the effect for enlarging
the range for suitable sealing and thus reducing exten-
sively the reject rate of sealing on practical use.

The effect may be further divided depending on
the selected sealing resin layers into a property group
20 for providing a sealing part excellent in fusing ability
accompanied with oil resistance and heat resistance or a
property group for providing a film excellent in low
temperature heat shrinkability, and the effect for
improving the sealing performance which is common in both
25 property group should be noted.

The sealing mode on packaging in the art
comprises first conducting sealing by heat fusion of the
opening part of a cylindrical bag having a content under

1 a state to ensure that reduced pressure is accomplished
also within the bag in a vacuum chamber and then pressure
in the vacuum chamber is raised up to atmospheric
pressure. At this time, the bag is deformed and
5 contacted tightly to the content by the pressure of air
so that the profile of the external shape of the content
will appear clearly, and such deforming force will act to
deform or break the unsolidified part of the afore-
mentioned sealing by heat fusion. A period of time
10 sufficient for solidifying the fused seal is incorporated
in a time required for sealing in the art. The time
required for sealing reached about 25% of the total time
required for packaging.

In the packaging by sealing in the afore-
15 mentioned fashion, the film of this invention has
preferably a heat resistant crosslinked polyolefin type
resin layer arranged on the surface layer in the side in
which the film touches directly a sealing bar and a resin
heat fusible at low temperature arranged on the interior
20 surface sealing resin layer which will control the
substantial fusing. That is to say, it may be considered
ideal to produce the relationship that even if the
interior surface side reaches the heating temperature
where fusing proceeds satisfactorily, the surface layer
25 is scarcely molten or at least does not reach such a
heated state as to press a fluidizingly deformed grooved
damage by the heat sealing bar.

In other words, specifically in the case of

1 this invention, even if, for instance, a crosslinked
ethylene-vinyl acetate copolymer is used as the surface
resin layer, there can be approached the aforementioned
ideal by utilizing directly the very non-fluid property
5 of the crosslinked resin even if the resin reaches the
temperature at the upper limit where it can keep heat
resistance, that is, the temperature exceeding the
crystalline melting point. When a crosslinked ethylene-
 α -olefin copolymer having a high crystalline melting
10 point such as 120°C or more, it will be easier to form
the aforementioned state by the increased difference of
the crystalline melting point as compared with that of a
resin used as the sealing resin layer as well as the
increased heat resistance of the aforementioned cros-
15 slinked resin (corresponding to sample No. 28 in Example,
Comparative Examples 1 and 2).

Therefore, it corresponds to the use of sealing
condition at relatively low temperature condition side
for the surface layer among the sealing resin layer
20 within the integral laminated film. Accordingly, the
sealing part solidifies at least at the surface side by
cooling in a short time, resists the film deforming force
applied on raising the pressure again up to atmospheric
pressure and reduces extensively a period of time
25 required for solidification by cooling. That is the so-
called "reduction of sealing time" herein used and leads
directly to the reduction of the time required for
packaging.

1 In the same manner, "reduction of reject rate
of sealing" herein used will be explained below.
Generally, film fusing at a sealing part is preferably
carried out between two flat films positioned opposedly.
5 However, the opening parts of bags continuously conveyed
are not always a pair of flat films but rather folded in
small wave shapes, and sealing is often carried out in
such a state as to press directly the folded films.
Therefore, the sealed part will inevitably cause the
10 increased reject rate of sealing such as break of
vacuum.

To the contrary, if the sealing resin layer of
the film of this invention has a range of suitable fusing
at a lower temperature as mentioned above, the shape of
15 the surface side of the film is maintained by the afore-
mentioned heat resistance, so that the folded sealing
part even around the center is satisfactorily within the
temperature range of compatible fusing and sealing
pressure is also applied to the part. Consequently, the
20 condition for suitable sealing of the sealing resin is
satisfied and the tight sealing between the sealing resin
layers proceeds.

Fig. 7 corresponding to Example, Comparative
Example 2 is a diagram from which a resin used as the
25 aforementioned sealing resin layer is judged and also a
demonstration of the preferred embodiment of this inven-
tion.

In Fig. 7, the regions illustrated by the

1 plotting with marks ⊙ or ○ generally correspond to the
regions of the region species and the composition useful
for "reduction of the time required for sealing" and
"reduction of reject rate of sealing" provided that the
5 aforementioned surface layer is used. Further, the
diagram indicates that the region is a part represented
by any one of the resins of an ethylene- α -olefin
copolymer resin (resin A) having a density of 0.88 - 0.93
and a crystalline melting point of 110 - 130°C, a mixed
10 resin comprising 60% by weight or more of said resin A
and 40% by weight or less of an ethylene- α -olefin
copolymer elastomer (resin B) or a mixed resin comprising
40% by weight or more of said resin A, 5 - 40% by weight
of said resin B and 55% by weight or less of an ethylene-
15 vinyl acetate copolymer resin (resin C), in which the
percentages of the components in said mixed resins amount
to 100% in total.

Fig. 6 corresponding to Experimental Example 6
illustrates the results from the experiment for re-
20 examining the aforementioned resin as the surface layer
from another standpoint that when the PVDC layer is used
as the core layer, the resin maintains the essential
adhesive strength with the core layer. That is, in Fig.
6, the axis of abscissa represents the vinyl acetate
25 content (% by weight) in the resin, the axis of ordinate
in the left side represents the adhesive strength with
PVDC (g/15 mm of width), and the axis of ordinate in the
right side represents the crystalline melting point (°C)

1 of the resin. Plotting with empty circles ○ (co-extruded
and uncrosslinked) and black-pained circles ● (co-
extruded and 5 Mrad dosed) represent the relationship
between the vinyl acetate content and the adhesive
5 content, and plotting with triangles △ represents the
relationship between the vinyl acetate content and the
crystalline melting point, respectively. At the parts
corresponding to 0% of the vinyl acetate content, three
ethylene- α -olefin copolymers having different crystalline
10 melting points are applied to A₀, A₃ and A₅.

Difference between the two kinds of circles
○ and ● in Fig. 6 represents the increase of adhesive
strength at the bonded part with the PVDC layer.
Crosslinking efficiency at a constant dosage is generally
15 considered to be proportional to the vinyl acetate
contents. Accordingly, there can be anticipated in
principle with the phenomenon that adhesive strength
increases in the region of the vinyl acetate of 13% by
weight or more in Fig. 6. However, it is extraordinarily
20 found that the increase of the adhesive strength in the
side of the lower vinyl acetate content of less than 13%
unexpectedly corresponds in its absolute value of the
adhesive strength with the increase shown by the un-
crosslinked EVA having a vinyl acetate content of about
25 13 - 20%.

The aforementioned phenomenon is effectively
utilized in this invention. In other words, in order to
maintain the adhesive strength of PVDC with a core layer,

- 1 it is generally considered necessary to use a specific resin such as EVA, EEA (polyethylene ethyl acrylate), EAA (polyethylene acrylic acid) and the like as an adhesion layer or as an adjacent layer to the core layer.
- 5 However, it is difficult to maintain the other properties such as heat resistance (crystalline melting point), oil resistance, heat shrinkability, and the like at high levels while maintaining the adhesive strength according to the conventional technics. Therefore, if heat
- 10 resistance at a higher temperature side exceeding about 90°C, it is necessary to provide a layer having a further higher melting point such as a layer of an ethylene- α -olefin copolymer resin or the like. But the resin is poor in the adhesive strength with the PVDC layer, and it
- 15 cannot be inevitable to provide another EVA layer having a high vinyl acetate content between the surfaces of the two, which consequently limit the quality design of the whole laminated film.

The significance represented by Fig. 6 and

20 useful in this invention consists in that even if an ethylene- α -olefin copolymer having a high crystalline melting point (vinyl acetate content, 0%) is used as a surface layer, an adhesive strength in the level of practical use can be principally obtained by providing

25 the copolymer adjacent to the core layer, and an EVA layer having a relatively high crystalline melting point (a low vinyl acetate content) can be used on providing an adhesion layer, so that the heat resistance and oil

1 resistance of the whole laminated film can be improved.
Further, to be noted is the value of the adhesive
strength increased by the co-extrusion-crosslinking in
the neighborhood of a vinyl acetate content of 13 - 20%
5 by weight. The high adhesive strength is an effect which
could not be obtained without any deterioration of the
PVDC layer, and the laminated film having a strong
bonding between surface layers can be obtained. These
are excellent effects produced by the crosslinking
10 according to this invention.

A further preferred embodiment corresponds to
Table 3 in Experimental Example 3 and relates to a
preferred embodiment of the PVDC layer used as a core
layer. This core layer controls principally the oxygen
15 gas barrier property of the laminated film and generally
arranged in a state containing a plasticizer and a
stabilizer in an amount of 2 - 4% by weight. The core
layer has a problem to lower the oxygen gas barrier
property by the yellowing by the irradiation of electron
20 rays to deteriorate or decompose the transparent quality
of a content. This invention restricts the transmittance
of electron rays to reduce the deterioration or yellowing
to the minimum, but the deterioration or yellowing of
PVDC cannot be completely avoided.

25 According to the result listed in Table 3, in
order to eliminate the deterioration or yellowing of the
core layer to the minimum, when PVDC is a vinylidene
chloride-vinyl chloride copolymer, the vinyl chloride

1 content is preferably in the range of 10 - 25% by weight,
and when PVDC is a vinylidene chloride-methyl acrylate
copolymer, the methyl acrylate content is preferably in
the range of 3 - 15% by weight.

5 In general, when the level of oxygen gas
barrier property is desired to be enhanced, the
vinylidene chloride-methyl acrylate copolymer is
preferably selected.

The b value referred herein is an index of a
10 color tone of a PVDC layer having been processed to a
thickness of 100 micron as an object and represents the
value measured in accordance with JIS Z 8729. The b
value of 17 or less is an upper criterion for satisfying
the required quality in which the content (raw meat)
15 within the package are looked clearly.

Another embodiment is the one which is obtained
from the standpoint of economy for manufacturing a co-
extruded laminated film and thus has a little different
appearance from the aforementioned embodiments for
20 satisfying the required quality at a high level.

That is to say, there have been investigated
for a long time many ideas for preparing a multi-layer
film in which resins compatible with the purposes of
respective layers have been laminated to exhibit the best
25 performance in laminated films. However, when the multi-
layer film is processed into a laminated film by a co-
extrusion method of intra-die lamination, it is un-
economical technically and thus undesirable to carry out

1 co-extrusion of the multi-layer film comprising 6 layers
or more because of the necessity of the arrangement space
of an extruder and the laminating structural space within
a die. Accordingly, it is also necessary to reduce the
5 number of layers and thus the kinds of resins used or to
combine two or more of the resin species of which
properties are compatible with each other so that an
extruder can be used for two or more layers to reduce the
number of extruders used.

10 From such standpoint, in the film of this
invention comprising laminating respective resin layers
in the sequence of (II)/(I)/(III)/(IV) or (II)/(II)'/(I)/
(III)/(IV), if resins in the same kind which can be
commonly used for the layers (II) and (IV) can be
15 provided with one extruder, a laminated film comprising 4
- 5 layers can be conveniently manufactured by 3 - 4
extruders. Alternately, if a resin which may be commonly
used for the layers (II)' and (III) is further used, a
laminated film comprising 4 - 5 layers can be manufac-
20 tured with three extruders.

A further embodiment relates to an application
most suitable to the film of this invention, the film
thickness for satisfying the required quality for the
application and the layer construction with the thickness
25 (corresponding to Tables 6-A and B in Example, Compara-
tive Example 1). As compared with the same kind of
commercially available film, it can be found that the
film of this invention is a film which has required main

- 1 properties all in high levels and accomplishes completely
the improvement of packaging performance as the required
quality in current market (see Table 11 for Example,
Comparative Example 5).
- 5 A further embodiment relates to a preferred
supplying shape of the cylindrical film of this inven-
tion. That is to say, cylindrical laminate co-extrusion
is conducted, and the product is subjected to inflation
orientation and directly rolled up to form a seamless
10 cylindrical laminated film. The seamless cylindrical
laminated film can be sealed tightly only by bottom
sealing and top sealing. This is a desirable film
because it has only two parts to be sealed and thus
producing a fewer reject rate at the sealing parts.
- 15 However, if the seamless cylindrical laminated film has a
small diameter, the production efficiency on film
formation is low and the cost will be heightened. In
such a case, a wide seamless cylindrical film is first
produced and folded flatly. Then, a bottom part is
20 provided to the film so as to have a required width, and
the film is cut into pieces by a side sealing method.
Thus, the cylindrical laminated film having a small
diameter can be economically manufactured.

Table 11 corresponding to Example, Comparative
25 Example 5 illustrates the results of classification of
the qualities and performance of the film of this inven-
tion with reference to quality level in comparison with
the currently available film in the art. Table 11 also

1 proves the property of the explanation of the contents of
this invention, because almost of the items of the above-
mentioned evaluations, of which items have been divided
into small classes of items, are listed in combination in
5 this table and can be evaluated in the same time.

As apparent from the results listed in Table 11,
the quality level of the film of this invention typified
by the sample Nos. 17 and 28 can be said to satisfy the
high quality levels in many items as compared with those
10 of commercially available films. Oil resistance, heat
resistance and shrinkability also reach certain levels.
It can be found more preferable to use the sample Nos. 34
and 52 for packaging processed meat which requires boiling
and the sample No. 39 for packaging raw meat which needs
15 high level of heat shrinkability at lower temperature.

The term "ethylene- α -olefin copolymer resin"
having a density of 0.88 - 0.93 (g/cm³) and a crystalline
melting point of 110 - 130°C" used in this invention means
a copolymer resin of ethylene and an α -olefin having 4 -
20 18 carbon atoms such as 1-butene, 1-pentene 4-methyl-1-
pentene, 1-hexene, 1-octene or the like.

The term "ethylene- α -olefin copolymer elastomer"
means a thermoplastic elastomer having a density of 0.91 -
0.85 (g/cm³) and a Vicat softening point (measured in
25 accordance with ASTM D 1525 with a load of 1 kg) of 80°C
or less and a rubber-like substance of a copolymer of
ethylene and an α -olefin having 3 - 8 carbon atoms such as
propylene, 1-butene, 1-hexene, 1-heptene, 4-methyl-1-

- 1 pentene, 1-octene or the like.

Further, the term "polyvinylidene chloride type resin (PVDC)" used in this invention means a copolymer resin obtained from vinylidene chloride and a monomer
5 copolymerizable therewith (e.g., vinyl chloride, methyl acrylate or the like).

The term "gel fraction" used in this invention means a gel fraction obtained by the following operations in accordance with ASTM D 2765.

- 10 (1) A sample (ca. 50 mg) taken from a prescribed position is weighed with a balance having a precision of 0.01 mg (S g);
- (2) A 150 mesh screen pouch manufactured by SUS which has preliminarily dipped into acetone for 24 hours
15 to remove oil and the sample are weighed with the balance (W1 g);
- (3) The sample is packaged with the pouch;
- (4) The sample packaged with the pouch is placed in a separable flask equipped with a condenser and retained
20 in boiling paraxylene for 1 - 2 hours;
- (5) The sample packaged with the pouch is dried in a vacuum drier until it reaches a constant weight;
- (6) The sample packaged with the pouch is weighed with the aforementioned balance (W2 g); and
- 25 (7) Gel fraction is calculated by the equation of
Gel fraction (% by weight) = $[1 - (W1 - W2)/S] \times 100$.

Attention should be paid on preparing the sample for measuring the aforementioned gel fraction with

1 reference to the followings:

When a specific layer of a laminate is intended to use as a sample, the layer should be peeled slowly with coating ethanol thereon; and

5 When a surface layer of a specific layer in a parison is intended to use as a sample, a piece of 10 mm x 20 mm is cut from a portion of the peeled specific layer having a good flatness and the surface layer is sliced into a thickness of about 20 micron with a
10 microtome for an optical microscope to make samples. It is also possible to slice a specific layer of an oriented film which has been peeled in the same manner as above and returned to a parison state by the heat shrinking
• treatment.

15 Evaluation methods and evaluation criteria used in this invention will be explained below.

(1) Film formability by drawing

An apparatus (or a method) illustrated in Fig. 5 was used. The pinch rolls 19 were driven at a speed of
20 7m/min, and film formation by drawing was attempted in order to reach a draw ratio in machine direction to transverse direction of 3/4. Evaluation was conducted with reference to the easiness of start-up of film formation by drawing, interconnected stability of a drawn
25 bubble and thickness spots of the film obtained.

Grade	Criteria
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◎	: Easy start-up; good interconnected stability of
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- 1 ○ bubble; thickness uniformity of film, within
 ±15%;
- Δ : No problem for start-up; drawing starting posi-
 tion vibrated finely; thickness uniformity
5 film, exceeding ±15% and within ±25%;
- × : Start-up with difficulty; drawing starting
 position is not fixed; thickness spot of film
 exceeds ±25%; and
- 10 : Drawing with difficulty; even if drawing was
 conducted, undrawn part remained in a zone or
 bubbles were rapidly broken.

(2) Oil resistance of interior surface

The seamless film thus produced was cut into a
predetermined length, and one end thereof was subjected
15 to heat sealing under a condition for obtaining a maximum
strength to make a bag.

On the interior side of the bottom sealed part of
the bag was coated lard, roast pork was pushed into the bag
until it abuts against the bottom sealing, and vacuum
20 packaging was conducted. Twenty packages thus prepared
were dipped into hot water at 90°C and taken up from the
hot water with a predetermined intervals, and the oil
resistance of interior surface was evaluated by inspecting
the presence of break at the bottom sealing part. The oil
25 resistance was considered good when the broken seals remain
within one. This evaluation was conducted with an antici-
pation of the package for use of boiling processed meat.

1	Grade	Criteria
	◎ :	good after 20 minutes,
	○ :	good after 5 minutes,
	Δ :	good after 1 minute
5	×	failed after 1 minute.

(3) Oil resistance of interior surface II

After suet was coated on the interior side of the bottom sealing part of the bag, raw beef was pushed into the bag until it abuts against the bottom sealing, and vacuum packaging was conducted. Twenty packages thus prepared were passed through hot water shower at 90°C over a period of time described below, and oil resistance of interior surface was evaluated by inspecting the presence of break at the bottom sealing part. The oil resistance was considered good when the broken seals remain within one. This evaluation was conducted with an anticipation of the package for use of chilled beef.

	Grade	Criteria
	◎ :	good after 12 seconds,
20	○ :	good after 8 seconds,
	Δ :	good after 4 seconds
	×	failed after 4 seconds.

(4) Reduction of time required for sealing

Using the bags prepared above, the suitable condition of impulse sealing in a vacuum packaging machine was selected based on strength. Then, meat in an

1 amount of 10 - 15 kg was placed in the bag, which was
then placed at the position as near as possible to the
sealing part of a vacuum packaging machine. Suet was
coated on the interior side of a part to be sealed, and
5 then vacuum packaging was conducted with changing the
cooling time after sealing as described below. After
dipping the sealed bag into hot water at 90°C for 4
seconds, evaluation was conducted referring to break of
vacuum, elongation at the sealed part, break, peeling of
10 the surface layer of the film and the like based on the
cooling time required for protecting the failure of the
film. The number of packages was 30.

Grade	Criteria
	◎ : no failure in 1 second of cooling time;
15	○ : failure did not disappear until cooling time was prolonged to 2 seconds;
	△ : failure did not disappear until cooling time was prolonged to 3 seconds;
20	× : failure did not disappear even if cooling time was prolonged to 3 seconds.

(5) Reject rate of sealing

Using the bags prepared above, a folding part
(double layered part) was intentionally made on one of
25 the films, and the condition of impulse sealing was
examined required for fusing completely with involving
the folding part. Then, raw meat in an amount of 10 - 15
kg was placed in the bag, which was then placed at the

1 position as near as possible to the sealing part of a
vacuum packaging machine. Suet was coated on the
interior side of a part to be sealed, and the opening
part of the bag was converged with hands and left opening
5 to make intentionally fine flexes with twisting. Then,
vacuum packaging was conducted under the condition of
cooling time for 2 seconds after sealing. After dipping
the packaged product into hot water at 90°C for 4
seconds, evaluation was conducted referring to break of
10 vacuum, elongation at the sealed part, break, peeling of
the surface layer of the film and the like referring to
the presence of the failure of the film. The number of
packages was 30.

Grade	Criteria
-------	----------

- | | | |
|----|-----|-------------------------------|
| 15 | ◎ : | within 1 of failed sealing; |
| | ○ : | 2 - 3 of failed sealing; |
| | △ : | 4 - 9 of failed sealing; |
| | × : | 10 or more of failed sealing. |

(6) Falling bag resistance at low temperature

20 After the bottom sealed part of the bag
prepared above was coated with suet, water in an amount
of 6 kg at about 2°C was charged into the bag. The
opening side of the bag was held with hands and the
bottom sealed part was dipped into hot water at 90°C for
25 4 seconds. Then, the opening was closed with a string.
The bag fallen from a height of 1 m onto a flat concrete
surface, and evaluation was conducted based on the number

- 1 of broken bags. The number of bags used in the test was 10.

Grade

Criteria

- 5 ◎ : within 1 of a broken bag;
 ○ : 2 - 3 of broken bags;
 Δ : 3 - 5 of broken bags;
 × : 5 or more of broken bags.

(7) Oil resistance at dints

A synthetic rubber dummy (having a length and a width of 30 cm, respectively and a thickness of 10 cm, on the surface of which are arranged semispherical dints having a radius of 1.5 cm with an interval of 10 cm) was placed into a bag prepared above and packed under vacuum. After coating suet on the exterior surface, the bag was dipped into hot water at 90°C for 4 seconds and then taken out. The presence of damages such as break or the like on the dints was examined to judge the total strength (heat resistance and oil resistance) of the film. Evaluation was carried out based on the break rate of the film.

Grade

Criteria

- 25 ◎ : within 10% of the break rate;
 ○ : 10% - 20% of the break rate;
 Δ : 20% - 50% of the break rate;
 × : more than 50% of the break rate.

1 (8) Color tone (b value) of PVDC

After a film was shrunk at a temperature of 70°C or more, only PVDC layers having been peeled and taken out were layered to a thickness of $100 \pm 5 \mu$ and placed on a white board. The b value was measured with a reflecting light in accordance with JIS Z 8729 to judge the color tone. A mineral oil has been coated on the interfaces between the PVDC layers. The larger the b value is, the more extensive the yellowing becomes.

10 Grade Criteria

- ◎ : 15 or less of the b value;
- : 15 - 17 of the b value;
- Δ : 17 - 20 of the b value;
- × : more than 20 of the b value.

15 (9) Transparency of the film

A film was placed on a cylinder having a bottom, the interior surface of which was lined with a black cloth for absorbing light, and the L value was measured with a reflecting light in accordance with JIS Z 8729. The larger the L value is, the more whitish the film is.

Grade Criteria (the L value)

- ◎ : 7 or less;
- : more than 7 and within 8;
- 25 Δ : more than 8 and within 9;
- × : more than 9.

1 (10) Transparency of the film after shrinking

A film was dipped in a hot water bath at 90°C for 4 seconds and shrunk under a relaxed state. After moisture on the surface had been wiped off, the haze of
5 the film was measured in accordance with ASTM D.1003 to evaluate the transparency.

Grade Criteria (Haze)

- © : 15% or less;
○ : more than 15% and within 25%;
10 Δ : more than 25% and within 40%:
x : more than 40%.

(11) Heat shrinkability and heat shrinkability at low temperature

A film having been cut into a square of 10 cm
15 in length and width was dipped in a hot water at 90°C referring to heat shrinkability or at 75°C referring to heat shrinkability at low temperature for about 4 seconds and shrunk under a relaxed state. The shrinkage factor was obtained by averaging shrinkage factors in length and
20 width based on the size at initiation.

Grade Criteria (Shrinkage factor)

- © : 30% or more;
○ : 20% or more and less than 30%;
Δ : 15% or more and less than 20%;
25 x : less than 15%

(12) Oil resistance on the exterior surface of the film

A film was spread in tension over a wooden

- 1 frame, and the exterior layer surface was coated with
lard. Then, the film was dipped together with the wooden
frame into hot water at 90°C and taken out after the
intervals of time mentioned below. The presence of
5 damages such as swelling of the exterior layer, whitening
or the like was examined to evaluate the oil resistance
of the exterior surface of the film.

Grade	Criteria
-------	----------

- | | |
|----|-----------------------------|
| | ◎ : good after 20 minutes; |
| 10 | ○ : good after 5 minutes; |
| | △ : good after 5 seconds; |
| | × : failed after 5 seconds. |

(13) Ply separation resistance

A film as cut into a shape of about 30 cm in
15 length and width, and lard was coated on the both ex-
terior and interior surfaces and ends. Then, the film
was dipped in a relaxed state into hot water at 90°C for
20 minutes and then taken out. The presence of bubble-
like ply separation in the film and ply separation at the
20 end parts of the film were examined to carry out evalua-
tion.

Grade	Criteria
-------	----------

- | | |
|----|--|
| | ◎ : no separation over all surfaces of the film; |
| | ○ : partial separation at the ends of the film; |
| 25 | △ : separation at the ends or partial bubble-like
separation; |
| | × : separation at the ends or bubble-like
separation. |

- 1 (14) Maintenance rate of oxygen barrier property after
flexing with twisting of the film

A film was dipped in a relaxed state into hot
water at 90°C for 4 seconds and shrunk. Then, the GELBO
5 test in accordance with MIL STD. B-131 was repeated 100
cycles at 0 - 2°C, and the oxygen gas penetrating rates
before and after test were measured in accordance with
ASTM D3985. The penetrating rates were compared, and the
strength of the PVDC layer against the flexing with
10 twisting was judged. If the increase of the penetrating
rate was within 30%, judgement of good was given.

Evaluation was carried out by the percentage of good
products. The number of films tested was 20.

Grade	Criteria (defective rate)
15 © :	within 10%;
○ :	more than 10% and within 25%;
Δ :	more than 25% and within 50%;
x :	more than 50%.

- (15) Maintenance rate of oxygen barrier property after
20 rough treatment under severe conditions

A synthetic rubber dummy (having 30 cm in
length and width, respectively, and 20 cm in thickness,
all tops and edges of which were rounded in a curvature
radius of 2 cm and on the whole surfaces of which are
25 arranged semispherical extrusion having a radius of 3 cm
with an interval of 2 cm) was packaged under vacuum with
a bag prepared above and passed through hot shower at

1 90°C. The bag was placed into a octahedral rotary drum
lined with a corrugated board. The drum was rotated 200
times at 0 - 2°C. Then, the film was peeled off, and the
oxygen gas penetrating rate was measured in the same
5 manner as in (14) and used as judgement of the strength
of the surface layer against rubbing with the exterior
surface. The film as partly drawn by the extrusions on
the dummy, so that the increase of oxygen penetrating
rate within 50% of that calculated from the average
10 shrinkage factor were judged good, and evaluation was
carried out with the percentages of good products.

Grade Criteria (Defective rate)

- ⊙ : within 10%;
○ : more than 10% and within 25%:
15 Δ : more than 25% and within 50%;
x : more than 50%.

(16) Heat resistance of films

Exterior surface side of a film spread in
tension over a wooden frame was touched softly with a hot
20 plate having a radius of 40 mm and heated to 200°C. The
presence of a hole at the contact part was examined with
a naked eye. The heat resistance of the film was
evaluated by judging the film having no hole good and the
one having a hole defective. The number of the film
25 tested was 20. This evaluation was carried out with
anticipation of checking the pinholes which tend to
generate in the neighbourhood of the sealing part on

1 sealing when the film is heated to high temperature.

Grade Criteria (Hole defective rate)

◎ : within 10%;

○ : more than 10% and within 25%;

5 Δ : more than 25% and within 50%;

x : more than 50%.

Experimental Example 1

This experiment is intended to examine the effects of the dosage distribution (depth) and dose
10 (strength of irradiation) of electron rays on the film of this invention.

In this experiment, films were prepared by changing electron beam irradiating methods and irradiation conditions with a film producing apparatus
15 illustrated in Fig. 5, and evaluation was carried out referring to heat resistance and oxygen barrier property after flexing with twisting.

In this experiment, films were prepared by changing electron beam irradiating methods and irradiation conditions with a film producing apparatus illustrated in Fig. 5, and evaluation was carried out referring to heat resistance and oxygen barrier property after flexing with twisting.

First of all, preparation methods of films are
25 explained below. In Fig. 5, a parison comprising four layers was extruded with three extruders 1 - 3, drawn at a speed of about 7 m/min to make a cylindrical parison

1 having a flat width of 115 mm. The parison comprised sequentially from its exterior side EVA (having a vinyl acetate content of 13.5% by weight)/PVDC (a vinylidene chloride-vinyl chloride copolymer resin having a comonomer
5 component derived from the vinyl chloride monomer in the resin of 17% by weight)/EVA (having a vinyl acetate of 13.5% by weight)/a sealing resin layers, which layers had a thickness of 275 μ /65 μ /225 μ /165 μ . As the afore-mentioned sealing resin, an ethylene- α -olefin copolymer
10 resin (very-low density polyethylene: density, 0.906; crystalline melting point, 118°C; trade name, NUC-FLX manufactured by NIPPON UNICAR Co.) was used. The parison was irradiated with electron rays using an electron beam irradiating apparatus 8. The electron beam irradiating
15 apparatus used in this experiment was two kinds of apparatuses, that is, ELECTROCURTAIN[®] (non-scanning type) manufactured by ENERGY SCIENCE INC. and a scanning type electron beam irradiating apparatus manufactured by NISSIN-HIGH VOLTAGE CO. Irradiation crosslinking was
20 carried out with changing dosages as shown in Table 12 by the use of these two electron beam irradiation apparatuses. The crosslinked parison was introduced into a heating bath 17 illustrated in Fig. 5, heated to a temperature of 80°C and subjected to an inflation biaxial orientation treatment to draw the film to a machine direction
25 of about 3 times and a transverse direction of 4 times, respectively, of their original sizes. The film having a flat width of 460 mm and an average thickness of about

1 60 μ was prepared in a length of 300 m and rolled round a
bobbin. For comparison, a further film was prepared
without irradiation.

The start-up of drawing was accompanied with
5 difficulty in some degrees in the case of sample Nos.
101, 108, 109, 110 and 116 in Table 12. (Difficulty was
due to that these samples were irradiated only in low
levels or nothing.)

Next, the film was left standing while it was
10 rolled round the bobbin for 3 days and then unrolled into
a film for 10 days at room temperature. Then, heat
resistance of the film was evaluated using a part of the
sample having a thickness of $60 \pm 5 \mu$ in the manner
described above. A run of twenty evaluation was
15 conducted. Also, the film was dipped in a relaxed state
into hot water at 90°C for 4 seconds and shrunk. Then,
retention of oxygen gas barrier property after flexing
with twisting of the film was evaluated in the manner
described above. A run of twenty evaluation was
20 conducted to calculate the non-defective rate of the
film.

The relationship between samples and the
irradiation conditions and the non-defective rates
obtained by the aforementioned evaluation were listed in
25 Table 12. Fig. 9 illustrates the plotting of non-
defective rates to the dosages.

In Fig. 9, empty marks mean the plottings of
experimental results using a modified non-scanning type

- 1 electron beam irradiation apparatus which was used in
this invention, in which empty circles ○ illustrate the
heat resistances of films and empty triangles
illustrate the oxygen gas barrier properties after
5 flexing with twisting of films. Black-painted marks mean
the plottings of experimental results using a conven-
tional scanning type electron beam irradiation apparatus,
in which black-painted circles ● illustrate the heat
resistances of films and black-painted triangles ▲
10 illustrate the barrier properties after folding of films.

The dosage distribution in the direction of
depth using the modified non-scanning type electron beam
irradiation apparatus which was practically used in this
experiment was illustrated by a solid line based on the
15 dosage at the surface as 100% in Fig. 1. The dosage
distribution using the conventional scanning type elec-
tron beam irradiation apparatus was illustrated by a
broken line 1. (Measurement was described in Experi-
mental Example 2.) It can be understood from Fig. 1 that
20 the modified non-scanning type electron beam irradiation
apparatus which was used in this invention extensively
attenuated dosage at a depth of a sample and thus
electron rays does not penetrate a depth of a sample.

According to the result shown in Fig. 9, in the
25 case of the conventional method (black-painted marks)
crosslinking effect increases rapidly from about 4 Mrad
and reaches its maximum level at about 6 Mrad. But large
dosage of electron rays is irradiated also to the PVDC

1 layer, so that deterioration of the PVDC becomes remark-
able, and a half of the PVDC becomes defective at about 3
Mrad where no crosslinking effect appears. Therefore, it
is impossible to select any appropriate range of exposed
5 dose in which irradiation (crosslinking) effect can be
taken without the deterioration of the PVDC layer.

On the other hand, Fig. 9 indicates that
according to the process of this invention (plotting with
empty marks), development of the crosslinking effect
10 remains at a low level and exposed dose of about 7 - 10
Mrad is required for obtaining the crosslinking effects
at a maximum level, but the dosage irradiated on the PVDC
layer is very small and the deterioration of the PVDC at
the same dose level is also reduced remarkably, so that
15 it is possible to select an appropriate range of exposed
dose for remaining the deterioration of the PVDC layer at
a minimum level while maintaining the crosslinking effect
at a high level.

Table 12

Sample No.	Electron beam irradiation apparatus used	Condition		Non-defective rate (%)	
		Acceler- ation voltage (KV)	Dosage (Mrad)	Heat resis- tance of film	Oxygen barrier pro- perty after flexing with twisting of film
101	Electrocur- tain® (non- scanning type, Titanium foil modified) manufactured by ENERGY SCIENCE INC.	200	3.5	0	95
102			5	75	100
103			6	90	100
104			7	95	100
105			8	100	100
106			10	100	95
107			12	100	90
108	Scanning type electron beam irradiation apparatus, manufactured by NISSIN HIGH VOLTAGE CO. LTD.	500	1	- *1	95
109			2	- *1	80
110			3	0	60
111			3.5	55	45
112			4	80	40
113			5	95	15
114			6	100	- *1
115			8	100	- *1
116	No dose of electron ways			0	100

*1 Not evaluated

1 Experimental Example 2

This experiment is intended to illustrate several dosage distribution referring to irradiating electron rays in the film of this invention and to
5 explain the importance of selecting the dosage distribution (depth of irradiation and size of crosslinking degree) to the film.

The dosage distribution is obtained by irradiating many layers of an EVA film (having a vinyl acetate
10 content of 13.5%) having a thickness of 10 μ under a condition of irradiating with an apparatus of which dosage distribution is intended to be examined and then measuring with boiling xylene the residual gel fraction of the film as the size of crosslinking degree.

15 The construction of the cylindrical parison proposed to the experiment is sequentially from the exterior side EVA (having a vinyl acetate content of 13.5% by weight)/PVDCX (a vinylidene chloride-vinyl chloride copolymer resin having a comonomer component
20 derived from the vinyl chloride monomer in the resin of 17% by weight)/EVA (having a vinyl acetate of 13.5% by weight)/a sealing resin layers, which layers had a thickness of 275 μ /65 μ /225 μ /165 μ . The aforementioned sealing resin is a mixed resin of an ethylene- α -olefin
25 copolymer resin having a crystalline melting point of 120°C : ethylene- α -olefin copolymer elastomer : EVA (having a vinyl acetate content of 15% by weight) = 8 : 1 : 1.

1 Films are prepared in the same manner as in
Experimental Example 1. The relations between the
irradiation apparatus and the exposed samples are listed
in Table 1.

5 The dosage distribution in the direction of
depth using the modified non-scanning type electron beam
irradiation apparatus which was practically used in this
experiment was illustrated by a solid line based on the
dosage at the surface as 100% in Fig. 1. The dosage
10 distribution using the conventional scanning type
electron beam irradiation apparatus by applying a high
acceleration voltage of 500 kV was illustrated by a
broken line 1. The dosage distribution by applying an
extremely low acceleration voltage of 250 kV was
15 illustrated by a broken line 2. The dosage distributions
of the exposed samples (Nos. 117 - 122 and 152) were
illustrated as (a) to (f) and (m) in Fig. 2.

For the respective samples, evaluation was
carried out by the methods described herein referring to
20 film forming ability by drawing, yellowing of PVDC,
oxygen gas barrier property after rough treatment under
severe conditions, the barrier property after flexing the
film with twisting, heat resistance of the film and gel
fraction. The results are listed in Table 2. As for the
25 gel fraction, measurements were carried out for the whole
layers of a parison from which the crosslinked polyolefin
type resin layer (II) in the exterior surface side of the
parison had been peeled, the exterior layer of said layer

1 (II) and the exterior layer in the PVDC layer side of
said layer (II). The gel fraction gradient $[y/x]$ was
calculated from the partial gel fraction $[x]$ at the
exterior surface layer, and the partial gel fraction $[y]$
5 at the surface layer in the PVDC layer side and listed in
the table.

The samples illustrated by Nos. 117, 152, 118
to 120 (corresponding to the dosage distributions (a),
(m), (b), (c) and (d) in Fig. 2, respectively) in Table 2
10 are arranged so that the effect of the change of the
dosages of electron rays having a constant penetrating
level in the direction of depth can be noted. Sample
Nos. 118, 121 and 122 (corresponding to the dosage
distribution (b), (e) and (f), respectively) are intended
15 to explain the effect of the irradiation of electron rays
having different penetrating levels in the direction of
depth.

First of all, the effect of penetrating levels
of electron rays in the direction of depth is explained.
20 The sample having the dosage distribution (b), film form-
ing ability by drawing and the heat resistance of which
are improved by crosslinking and barrier property of
which is also retained, is thus preferred. This is
probably due to that although the electron rays penet-
25 rates with sufficiently crosslinking the crosslinking
polyolefin type resin layer (II) into the bonding layer
between the layer (II) and the PVDC layer to cause
denaturation so as to increase adhesion, it gradually

1 attenuates and penetrates only central position of the
PVDC layer, which is irradiated with only a small dosage
on the PVDC layer and cause no deterioration. On the
other hand, the sample having the dosage distribution (f)
5 (No. 122), although it has a crosslinking effect, is
drastically deteriorated in the PVDC layer (in retention
rate of oxygen barrier property after flexing of film and
color tone of PVDC) and thus can not be used practically.
The reason is that the gel fraction gradient is 0.63, that
10 is, electron rays penetrates the depth and the PVDC layer
is also irradiated with a high dosage of electron rays to
cause deterioration. The sample having the dosage
distribution (e) (No. 121) exhibits a very interesting
phenomenon that electron rays does not penetrate into the
15 bonding part between the PVDC layer and the exterior
surface layer, which part is not denaturated by electron
rays and adhesive strength is not increased. Also
uncrosslinked part in the exterior surface layer remains
in the neighbourhood of the PVDC layer, which probably
20 makes the film too weak to endure external force.

Next, dosages are explained with reference to
electron rays having the same penetrating level in a
direction of depth. From the results obtained from the
samples of Nos. 117, 152, 118 to 120 listed in Table 2.
25 The dosage range suitable for the film of this invention
has a lower limit illustrated by dosage distribution (c)
(No. 119), in which the gel fraction is 20% by weight in
the whole crosslinking polyolefin type resin layer and

- 1 25% by weight in the exterior surface layer. If the
dosage is less than the lower limit described above, the
gel fraction is insufficient as illustrated by the dosage
distribution (d) (No. 120), so that properties including
5 film forming ability by drawing, heat resistance and
resistance to rough treatment under severe conditions are
not improved. The upper limit is illustrated by the
dosage distribution (m) (No. 152), in which the gel frac-
tion is 60% by weight in the whole crosslinking
10 polyolefin type resin layer and 70% by weight in the
exterior surface layer. If the dosage is larger than the
upper limit, the gel fraction is slightly excessive as
illustrated by the dosage distribution (a) (No. 117), so
that film forming ability by drawing is less preferred.
- 15 From the above explanation, it can be said that
the range of dosage distribution suitable for the film of
this invention is illustrated by (m), (b) and (c) (sample
Nos. 152, 118 and 119, respectively) in Fig. 2. If it is
expressed by the penetrating level of electron rays, the
20 gel fraction gradient of the crosslinking polyolefin type
resin layer (II) is 0.6 or less and the bonding part
between the layer (II) and the PVDC layer (I) is a bond-
ing part which has been denaturated with electron rays.
If it is expressed by dosage, the gel fraction of the
25 whole layer (II) is in the range of 20 - 65% by weight
and the gel fraction at the exterior surface layer [x] is
in the range of 25 - 70% by weight.

The range of the gel fraction gradient will be

1 explained again in Experimental Example 5 with reference to the aforementioned layer (II) comprising two layers.

Table 1

Electron beam irradiation apparatus used /	Condition		Irradiation pattern (Marks in Fig. 2)
	Acceleration voltage (KV)	Dosage (Mrad)	
Electrocurtain [®] (non-scanning type, Titanium foil modified) manufactured by ENERGY SCIENCE INC.	200	13	(a)
		12.5	(m)
		10	(b)
		5	(c)
		3	(d)
	175	12.5	(e)
500 KV Scanning type, manufactured by NISSIN-HIGH VOLTAGE CO. LTD.	250 ^{*2}	9	(f)

*1 Dosage at the surface part of the cylindrical parison

*2 If it will be further lowered, output will be too decreased to use it industrially. In addition, the dosage distribution is too short against the depth to apply for this invention.

Table 2

Sam- ple No.	Dosage distri- bution (Marks in Fig. 2)	Gel fraction of crosslinking poly- olefin type resin layer (% by weight)			Gel fraction gradient [y/x]	Film forming ability of drawing	Color tone of PVDC (b value)	Retention rate of oxygen gas bar- rier pro- perty after rough treatment under severe condition	Retention rate of oxygen gas barrier property after flexing of film with twisting	Heat resis- tance of film
		Whole layer	Exterior surface layer [x]	Surface layer in the layer [I] side [y]						
117	(a)	62	73	31	0.42	Δ	⊙	⊙	⊙	⊙
152	(m)	60	70	28	0.40	o	⊙	⊙	⊙	⊙
118	(b)	50	61	20	0.33	⊙	⊙	⊙	⊙	⊙
119	(c)	20	25	5	0.20	o	⊙	⊙	⊙	o
120	(d)	5	11	1.0	0.09	Δ	⊙	Δ	⊙	x
121	(e)	44	70	0.4	<0.01	o	⊙	x *1	⊙	⊙
122	(f)	47	56	35	0.63	⊙	x	x	x	⊙

*1 At the initial stage of rough treatment, under severe condition, the exterior layer is separated from the PVDC layer.

1 Experimental Example 3

This experiment is intended to explain the significance of the selection of the kind of PVDC in this invention.

5 This experiment was carried out in the same manner as in Experimental Example 2 except that the composition of PVDC used as the core layer of the sample No. 118 was changed as follows. The PVDC's used were a vinylidene chloride-vinyl chloride copolymer resin and a
10 vinylidene chloride-methyl acrylate copolymer resin. In the vinylidene chloride-vinyl chloride copolymer resin, the content of the comonomer component derived from the vinyl chloride monomer in the resin was varied in 8 levels of 4, 6, 8, 10, 17, 25, 28 and 30% by weight, and
15 in the vinylidene chloride-methyl acrylate copolymer resin, the content of the comonomer component derived from the methyl acrylate monomer in the resin was varied in 6 levels of 1, 3, 10, 15, 18 and 20% by weight. The films thus prepared were evaluated by the evaluation
20 methods described herein with reference to the color tone (b value) of PVDC and oxygen barrier property after flexing of the film with twisting. The results are listed in Table 3.

According to the results shown in Table 3, in
25 the irradiation of electron rays having the dosage distribution (b) (Fig. 2), as the PVDC in order to avoid deterioration or yellowing which will be caused at the core layer there are preferably used a vinylidene

- 1 chloride-vinyl chloride copolymer resin, in which the
content of the comonomer component derived from the vinyl
chloride monomer in the resin is in the range of 10 - 25%
by weight, and a vinylidene chloride-methyl acrylate
5 copolymer resin, in which the content of the comonomer
component derived from the methyl acrylate monomer in the
resin is in the range of 3 - 15% by weight.

As explained above, it is very significant to
select suitably the PVDC used as the core layer. In
10 order to exhibit the effect of improving the film forming
ability by drawing and the effect of improving the film
properties to the maximum, it is necessary to irradiate
the polyolefin type resin layer as the surface layer to
the direction of its depth with electron rays in a
15 sufficient amount. However, in its case the core layer
is inevitably irradiated with electron rays. The
presence of PVDC which is relatively stable to electron
rays made possible to directly irradiate the surface of a
coextruded layer which has been considered impossible to
20 complete direct irradiation.

Table 3

Sample No.	PVDC used		Evaluation Result	
	Comonomer species	Ratio of VDC: comonomer	Oxygen barrier property after flexing film	color tone of PVDC
123	Vinyl chloride	96: 4	X	X
124		94: 6	X	Δ
125		92: 8	Δ	○
126		90:10	⊙	⊙
118		83:17	⊙	⊙
127		75:25	○	⊙
128		72:28	Δ	⊙
129		70:30	X	⊙
130	Methyl acrylate	99: 1	X	Δ
131		97: 3	⊙	⊙
132		90:10	⊙	⊙
133		85:15	○	⊙
134		82:18	Δ	⊙
135		80:20	X	⊙

1 Experimental Example 4

This experiment is intended to explain the construction method of the crosslinking resin layer which is one of the important points for accomplishing the film of this invention, that is, the effect of the processes for providing a crosslinking polyolefin type resin layer on the surface of a laminated film comprising a PVDC layer as the core layer on the properties of the laminated film obtained.

10 As the methods for constructing the crosslinking layer, there were used the following well-known methods;

a method according to Fig. 1 in Japanese Patent Application Publication No. 43024/83,

15 a method according to Japanese Patent Application Kokai (Laid-Open) No. 143086/76, page 4,

a method according to Figs. 6 and 7 of US Patent No. 3,821,182, and

a method according to Japanese Patent Application Kokaid (Laid-Open) No. 82752/83, pages 4 - 5, which methods were repeated as precisely as possible (sample Nos. 136, 137, 138 and 139, respectively).

As the electron beam irradiation apparatus, there was used a 500 kV scanning type irradiation apparatus manufactured by NISSIN-HIGH VOLTAGE CO. LTD. The dosage distributions applied to the films were those illustrated in Tables 3-A and 3-B as (g), (h), (i) and (j).

1 For comparison, a laminated film according to
Japanese Patent Application Publication No. 1295/86 was
prepared as a representative of uncrosslinked (unirradi-
ated) articles and listed in Table 4 as sample No. 140.

5 The structural features of the laminated films
prepared above are listed in Table 4.

 These films (sample Nos. 136 to 140) and the
film of this invention (sample No. 118) were evaluated by
the methods described herein with reference to film
10 forming ability by drawing, reject rate of sealing, color
tone (b value) of PVDC, oil resistance on exterior
surface, resistance to PLY (interfacial) separation and
oxygen gas barrier property after flexing of film
external with twisting. The results are listed in Table
15 5.

 According to the results shown in Table 5,
effect of improving film forming ability by drawing can
be exhibited by using the laminate comprising a cross-
linking resin layer. But if electron rays for cross-
20 linking irradiates the PVDC layer largely, the PVDC
layer is too extensively deteriorated to use it
practically even if a PVDC having a selected content of
the comonomer is used.

 On the other hand, in the films prepared by
25 laminating another layer on the crosslinked layer (sample
Nos. 136 and 139); resistance to PLY (interfacial)
separation cannot be guaranteed.

 Therefore, it can be said that the construction

- 1 method of this invention (sample No. 118), in which the whole layers having a sealing layer in the interior side are laminated by a co-extrusion method, and the surface layer of the laminate are moderately crosslinked, is an
- 5 excellent method for exhibiting satisfactorily properties of respective layers.

Table 4

Sam- ple No.	Layer construction of cylindrical film Exterior ← Interior layer	Characteristics of the process for construc- ting a crosslinked layer	Dosage distrib- ution (Marks in Fig. 3)
136	<p style="text-align: center;">Irradiation</p> <p style="text-align: center;">EVA (Vac. 10%)/PVDC^{*1}/EVA (Vac. 10%) (15 μ / 10 μ / 35 μ)</p>	<p>Process according to Jap. Pat. Appln Publ. No. 43024/83, Fig. 1; preceded by extruded inner EVA layer was irradiated with electron rays and crosslinked, and PVDC and EVA layers were laminated by melt-extruded coating method sequentially thereon.</p>	(g)
137	<p style="text-align: center;">Irradiation</p> <p style="text-align: center;">EVA (Vac. 10%)/PVDC^{*1}/EVA (Vac. 10%) (15 μ / 10 μ / 35 μ)</p>	<p>Process according to Japanese Patent Application Laid-Open No. 143086/76, page 4; after repetition of the above process and film formation, electron rays were irradiated over all layers of the film and crosslinking was conducted.</p>	(h)

- cont'd -

Table 4 (Cont'd)

138	<p>Irradiation</p> <p>LDPE (density 0.92) / PVDC^{*1} / LDPE (density 0.92)</p> <p>(15 μ / 10 μ / 35 μ)</p>	<p>(i)</p> <p>Process according to USP 3,821,182, Figs. 6 and 7; after intra-die laminated extrusion of LDPE/PVDC/LDPE, whole layers of the cylindrical parison were irradiated with electron rays and cross-linked.</p>	
139	<p>Irradiation</p> <p>Blend composition A^{*2} / EVA (Vac. 15%) / PVDC^{*1} / EVA (Vac. 15%) / Blend composition B^{*2}</p> <p>(13 μ / 2 μ / 10 μ / 2 μ / 33 μ)</p>	<p>(j)</p> <p>Process according to Japanese Patent Application Laid-Open No. 82752/83, page 4, right upper column, line 3 - page 5, line 8; interior layer blend composition B having been precededingly extruded was irradiated with electron rays and crosslinked, and co-extruded EVA/PVDC/EVA and blend composition A were sequentially laminated thereon by melt-extruded coating method.</p>	

- cont'd -

Table 4 (Cont'd)

140	L-LDPE ^{*3} / EVA (Vac. 20%) / PVDC ^{*1} / EVA (Vac. 15%) / L-LPDE ^{*3}			Process according to Japanese Pat. Appln. Publn. No. 1295/81, page 4; no irradiation.	
	(7 μ /	1 μ /	8 μ /	36 μ /	8 μ)

*1 Vinylidene chloride-vinyl chloride copolymer resin, in which a comonomer component derived from the vinyl chloride monomer in the resin is in an amount of 17% by weight.

*2 (Resin mentioned in *3) : EVA (having vinyl acetate of 10% by weight.)

*3 Linear low density polyethylene having a crystalline melting point of 120°C and a density of 0.920.

Table 5

Sample No.	Dosage distribution (Marks in Figs. 2 or 3)	Film forming property by drawing	Reject rate of sealing	Color tone (b value)	Oil resistance on exterior surface	PLY (interfacial separability)	Oxygen barrier property after flexing of film
118	(b)	⊙	⊙	⊙	⊙	⊙	⊙
136	(g)	⊙	Δ	⊙	x	x	⊙
137	(h)	⊙	x	x	o	⊙	x
138	(i)	o	x	x	⊙	o	x
139	(j)	o	Δ	⊙	Δ	x	⊙
140	Unirradiated	x	x	⊙	o	o	⊙

1 Experimental Example 5

This experiment is intended to explain specifically the creative content of the method for producing a crosslinked surface layer which is advantageous for
5 improving the film of this invention having a high crosslinking degree (gel fraction) without damaging the so-called film forming ability by drawing, and the effect thereof.

Experiment was carried out in the same manner
10 as in Experimental Example 2 to obtain a film of sample No. 117 (dosage distribution (a)). Experiment was also carried out in the same manner as above except that in the layer construction, the outermost part having a thickness of 170 μ in the interior side of the EVA layer
15 (vinyl acetate content, 13.5% by weight) having a thickness of 275 μ at the exterior layer is replaced with an EVA resin layer having a vinyl acetate content of 10% by weight, and the residual part having a thickness of 105 is replaced with an EVA resin layer having a vinyl
20 acetate content of 15% by weight to obtain the sample No. 141. The sample is formed in the same manner as in Experimental Example 1 by the use of an apparatus illustrated in Fig. 5, and specifically film was formed by the use of five extruders including another extruder in
25 addition to four extruders 1 - 3' illustrated in Fig. 5. The sample No. 141 was evaluated in the same manner as in Experimental Example 2 according to the methods described herein with reference to film forming ability by drawing,

1 yellowing of the PVDC layer, oxygen gas barrier property
after rough treatment under severe conditions, oxygen gas
barrier property after flexing of film with twisting,
heat resistance of film and the gel fraction of the
5 polyolefin type resin layer. The results are listed
together with those of the sample No. 117 in Table 14 for
comparison. The gel fraction in Table 14 was measured
for that [x] at the exterior surface layer and that [y]
at the surface layer in the layer (I) and listed together
10 with the gel fraction gradient [y/x].

In order to find the practical gel fraction
(crosslinking degree) to the direction of the depth in
the surface layer, a film having a thickness of 10 μ was
layered to obtain a laminate as a model sample. The
15 sample was subjected to irradiation with electron rays,
and then evaluation was carried out in the same way as
above. The results were illustrated as the distributions
of gel fraction (k) and (l) in Fig. 4. The difference of
the distributions of the gel fraction (k) and (l) under
20 the same dosage depends on the difference of the cross-
linking efficiencies of resins on irradiation. In other
words, in the sample No. 117 the surface layer is an EVA
(having a vinyl acetate content of 13.5% by weight) layer
and the distribution traces the curve of (k). In the
25 sample No. 141, the EVA having a vinyl acetate content of
10% by weight has a low crosslinking efficiency, so that
the gel fraction drops down relatively. On the other
hand, the intermediate surface layer comprising EVA

1 having a vinyl acetate content of 15% by weight has a
higher crosslinking efficiency, so that the distribution
shows a high value. Thus, the sample No. 141 forms the
distribution curve ① having a cleavage.

5 If such a phenomenon is examined from an aspect
of the change of film forming ability by drawing, the
failure of film forming ability by drawing in the sample
No. 117 will be improved to the maximum by the sample No.
141, as shown in Table 14. A part which has a partial gel
10 fraction of 73% by weight and is hardly drawn is present
in surface layer of the parison of the sample No. 117,
while in the sample No. 141 having the distribution ①
the excessively crosslinked part which is hardly drawn is
removed.

15 In conventional art, if the failure of film
forming ability by drawing illustrated by the distribution
① happened, dosage was lowered by controlling the irradi-
ation condition. But the whole distribution of dosage was
also lowered, and consequently the gel fraction was also
20 lowered. On the other hand, the creativeness of this
invention consists in that if the layer corresponding to
the excessive gel fraction is replaced with a resin having
a lower crosslinking efficiency, only the excessive
crosslinking part can be removed without levelling down
25 the whole gel reaction.

The difference of the crosslinking effect to the
same dosage depends on the relative values of the resins
to be used. That is, when an EVA having a vinyl acetate
content of 13 - 20% by weight of which PLY (interfacial)

1 adhesive strength is extensively increased by irradiation
of electron rays are used, a resin having a lower cross-
linking efficiency such as specifically an EVA having a
vinyl acetate content of 10 - 5% by weight, a low density
5 or very-low density linear polyethylene or linear low-
density polyethylene, a mixed resin of the two or a
sealing resin comprising three components according to
this invention is used. The group of resins having low
crosslinking efficiency exhibits very excellent properties
10 (e.g. thermostability, oil resistance, rub resistance,
toughness and the like) upon crosslinking compared with
those exhibited by the crosslinking of the EVA having a
vinyl acetate content of 13 - 20% by weight.

Based on the technical aspects the crosslinking
15 resin layer of this invention comprises two layers having
high and low crosslinking efficiency, respectively, of
which the one having low crosslinking efficiency is used
as the outermost surface layer.

Referring to the gel fraction gradient $[y/x]$ of
20 the sample Nos. 141 and 117, it shows a value of 0.42 in
the sample No. 117 and 0.57 in the sample No. 141, because
the crosslinking polyolefin type resin layer (II)
comprises two layers having different crosslinking
efficiency from each other. Thus, if two layers having
25 crosslinking efficiency are used for the layer (II), the
gel fraction gradient does not exceed a value of 0.63 at
the dosage distribution (\bar{f}) (sample No. 122) shown in
Table 2 in Experimental Example 2. Therefore, the film of
this invention can be characterized in that the gel

- 1 fraction gradient of the layer (II) is 0.6 or less. The partial gel fraction [y] of the surface layer in the PVDC layer side in the aforementioned layer (II) is 36% by weight even in the case of the sample No. 141 in which a
- 5 resin having a high crosslinking efficiency is used for the intermediate surface layer, at most 40% by weight or less. The sample No. 122 has a partial gel fraction [y] of 35% by weight, but the gel fraction gradient is 0.6 or more, so that electron rays penetrates into the PVDC
- 10 layer, which is thus deteriorated.

Table 14

Sam- ple No.	Distri- bution of gel fraction (Marks in Fig. 4)	Gel fraction in cross- linking polyolefin type resin layer			Gel fraction gradient [y/x]	Film forming property of drawing	Color tone of PVDC (b value)	Retention rate of oxygen gas barrier property after rough treatment under se- vere con- dition	Retention rate or oxygen barrier property after flexing of film with twisting	Heat resistance of film
		whole layers	ex- terior layer [x]	surface layer in layer (I) side						
141	①	59	63	36	0.57	⊙	⊙	⊙	⊙	⊙
117	②	62	73	31	0.42	Δ	⊙	⊙	⊙	⊙

1 Experimental Example 6

This experiment is intended to distinguish the adhesive strength of an EVA, an ethylene- α -olefin copolymer resin, three layered of which vinyl acetate contents are different from each other and a PVDC, by the irradiating electron rays or not.

By means of a conventional three layered well-known co-extruder equipment, a cylindrical parison having a three layer structure of EVA/PVDC/EVA could be formed by extrusion, an EVA having a vinyl acetate content of 15% by weight and a PVDC were fixedly supplied into an extruder for a interior layer and an extruder for a core layer, respectively. In an extruder for an exterior layer were supplied sequentially an ethylene- α -olefin copolymer resin A₅ (very-low density polyethylene: density, 0.900; crystalline melting point, 115°C; manufactured by Sumitomo Chemical Co., Ltd.) and EVA's having a vinyl acetate content of 5, 10, 13, 15, 20 and 25% by weight were sequentially supplied. A co-extruded cylindrical laminated parison having a flat width of 150 mm and a thickness of 30 μ /30 μ /30 μ was extruded and cooled rapidly to be taken out. To this parison was used a ELECTRO CURTAIN[®] manufactured by ENERGY SCIENCE INC., described in Table 1, and irradiation with electron rays was conducted at a acceleration voltage of 200 kV and a dosage of 5 Mrad (pattern © in Table 1). It was left standing for three days at room temperature together with a parison without irradiation

1 for comparison. After the parison was cut out into a
flat parison, the adhesive strength of the EVA layer in
the exterior layer side and the core layer was measured
by a constant speed tensile testing machine. The
5 measurement condition was the sample width of 15 mm, the
tensile angle of 180° and 500 mm/min of tensile speed.

Fig. 6 illustrates the aforementioned adhesive
strengths (g/15 mm width) classified by irradiating
electron rays or not, to the vinyl acetate content of the
10 resin used. The axis of abscissa in the right side is
crystalline melting point, and the value of the used
resin and catalogue values of used resins and two others
(measured by the DSC method) are illustrated. One of
these two resins are a low density polyethylene resin A₀
15 (density, 0.920; crystalline melting point, 108°C), and
the other is an ethylene- α -olefin copolymer resin A₃
(linear low density polyethylene: density, 0.923;
crystalline melting point, 122°C; trade name, Dowlex;
manufactured by DOW CHEMICAL CO.). The solid line in the
20 graph illustrates the adhesive strength of the PVDC layer
and the adjacent layer in the cylindrical surface side.
The empty marks mean the case without irradiation of
electron rays. The black-painted marks mean the case
with irradiation of electron rays. Empty circles
25 ○ illustrate the values of EVA, and empty squares □
illustrate the values of the ethylene- α -olefin copolymer
resin. Empty triangles Δ and chain line illustrate the
crystalline melting points of respective resins.

1 The difference of the empty circles O and
black-painted circles ● in Fig. 6 represents the increase
of the adhesive strength with the PVDC layer at folding
part by crosslinking. Generally, crosslinking efficiency
5 under the constant dosage is considered to be in proportion to the vinyl acetate content. Accordingly, in the relationship in Fig. 6, the phenomenon of increasing the adhesive strength in the region of the vinyl acetate content of 13% by weight or more may be anticipated.
10 However, it was extraordinarily found that in the region of lower vinyl acetate content side of less than 13% by weight the adhesive strength was remarkably increased, which corresponded to the value exhibited by the uncrosslinked EVA having a vinyl acetate content of about 13 -
15 20% by weight. Moreover, also in an ethylene- α -olefin copolymer resin (having a vinyl acetate content of 0% by weight) which will not usually adhere substantially to PVDC adhesive strength as high as in the EVA having a vinyl acetate content of about 13% by weight could be
20 obtained. (See the symbol ■ in Fig. 6)

Experimental Example 7

This experiment is intended to explain the effect of dosage of electron rays on the adhesive strength at the bonding part of the PVDC layer and the
25 adjacent layer thereof when a crosslinking layer is provided without deterioration of the PVDC layer by the irradiation of electron rays.

1 The methods for constructing the crosslinking layer without deteriorating the PVDC layer include methods

- ① irradiating after co-extrusion with a modified,
5 non-scanning type electron beam irradiating apparatus, as shown in Experimental Example 1 of this invention, and
② extra-die laminating by melt-extruded coating method after irradiating electron rays in accordance with the method of Fig. 1 of US Patent No. 3,741,253.

10 In this experiment, as the method ①, a parison comprising three layers was extruded by the three extruders 1 - 3 in Fig. 5, drawn out at a speed of 3 m/min to make a cylindrical parison having a flat width of 130 mm. The parison has a construction sequentially from the
15 exterior side of EVA (having a vinyl acetate content of 10% by weight)/PVDC (a vinylidene chloride-vinyl chloride copolymer resin having a comonomer component derived from the vinyl chloride monomer in the resin in an amount of 17% by weight)/EVA (having a vinyl acetate content of 15%
20 by weight) with a thickness of 275 μ /65 μ /390 μ . The parison was irradiated with electron rays by an electron beam irradiating apparatus 8. The electron beam irradiating apparatus and dosing condition used are listed in Table 13. The crosslinked parison as heated to a temper-
25 ature of 80°C in a heating bath 17, then subjected to inflation bi-axial orientation to three times machine direction and four transverse direction wide, and the film having a flat width of 520 mm and an average thickness of 61 μ

1 was formed in a length of 200 m and rolled round a
bobbin. For comparison, a film was also prepared without
irradiation. The sample Nos. 142 and 143 listed in Table
13 showed somewhat difficulty for the start-up of
5 drawing.

As the method ②, a cylindrical EVA (having a
thickness of 275 μ and a vinyl acetate content of 10% by
weight) was first prepared, and the parison was irradi-
ated with an electron beam irradiating apparatus and
10 dosing condition listed in Table 13. Immediately after
irradiation, a PVDC layer and an EVA layer were laminated
with the parison in accordance with the method illust-
rated in Fig. 1 of Japanese Patent Application Publi-
cation No. 43024/83 to make a cylindrical parison having
15 the layer construction from the exterior side of EVA
(having a vinyl acetate content of 15% by weight)/PVDC (a
vinylidene chloride vinyl chloride copolymer resin, in
which the content of the comonomer component derived from
the vinyl chloride monomer in the resin is 17% by
20 weight)/EVA (having a vinyl acetate content of 15% by
weight) with a thickness of 390 μ /65 μ /275 μ and a flat
width of 130 mm. Then, the cylindrical parison was
subjected to inflation bi-axial orientation treatment in
the same manner as in ① to make a film. A further film
25 was prepared for comparison without irradiation. The
sample Nos. 147 and 148 listed in Table 13 showed some-
what difficulty for the start-up of drawing.

Each sample was left standing while rolled

1 round the bobbin for three days at room temperature, then
the adhesive strength between the crosslinked EVA layer
and the PVDC layer was measured over all width of the
cylindrical film with a constant speed tensile testing
5 machine. The measurement was carried out under the
conditions of a sample width of 20 mm, a tensile angle of
180° and a tensile speed of 500 mm/min.

Fig. 8 illustrates the adhesive strength
measured above (g/20 mm width) plotted to the dosage of
10 electron rays separately for the irradiation methods of
① and ②, in which empty circles ○ represent the case
of this invention and black-painted circles ● represent
the case of conventional well-known method.

Table 13

Sample No.	Film forming method	Electron beam irradiating apparatus used	Condition	
			Accelara- tion volt- age (KV)	Dosage (Mrad)
142	①	No irradiation of electron beam		
143		ELECTRO-CURTAIN ^R . (Titanium foil modified non- scanning type), manufactured by ENERGY SCIENCE INC.	200	3
144				5
145				8
146				10
147	②	No irradiation of electron beam		
148		Scanning type electron beam irradiating apparatus, manu- factured by NISSHIN HIGH- VOLTAGE CO. LTD.	500	3
149				5
150				8
151				10

1 Example, Comparative Example 1

Following experiment was carried out to explain the appropriate constructions of layer and thickness for obtaining the film of this invention. That is, the apparatus (and the method) illustrated in Fig. 5 as used, and
5 twenty-eight kinds of films (sample Nos. 1 - 28) having the layer constructions and the gel fractions which are shown in the items (see Tables 6-A and 6-B) "layer construction of film" and "gel fraction of crosslinked polyolefin type resin layer", respectively, were formed.
10

Films were prepared in the same manner as in Experimental Example 1 in Fig. 5. First of all, a parison was formed with four extruders 1 - 3' for the sample Nos. 1 - 12, 14 - 16, 22 and 28; five extruders
15 for the sample No. 13; three extruders 1 - 3 for the sample Nos. 17 - 21, 23 - 27; and four layer extrusion was carried out for the sample Nos. 19 and 23, and five layer extrusion was carried out for all other samples. The modified non-scanning type electron beam irradiating
20 apparatus which as used in Experimental Example 1 was used as the electron beam irradiating apparatus, in which acceleration voltage was controlled based on the preliminarily calibrated relationship of acceleration voltage and dosage distribution (depth) regarding the thickness
25 of the polyolefin type resin layer (I) of each parison so that the dosage will be zero at around the center of the PVDC layer. For example, in the sample Nos. 1 and 3 having the same total parison thickness of 720 μ , the

1 thickness of the polyolefin type resin layer (I) is 120
and 300 μ , respectively, and thus acceleration voltage
was adjusted to 150 kV and 200 kV, respectively. After
crosslinking, all samples were subjected to inflation bi-
5 axial orientation treatment to ca. 3 times machine
direction and ca. 4 time transverse direction to form a
film having a prescribed layer thickness.

These films were left standing while rolled
round the bobbin for 7 days at room temperature, and then
10 evaluation was carried out by the methods mentioned
herein referring to film forming ability by drawing, heat
shrinkability, retention factor of oxygen barrier pro-
perty after rough treatment under severe condition, heat
resistance and oil resistance (on exterior surface and
15 dint), falling bag resistance at low temperature and heat
resistance of film. The results are listed in the
columns of results in Tables 6-A and 6-B.

The results in Tables 6-A and 6-B indicate the
followings. That is, the sample Nos. 1 - 5 relate to an
20 appropriate thickness of "crosslinking polyolefin type
resin" at the surface layer and the sample Nos. 6 - 9
relate to an appropriate crosslinking degree (gel frac-
tion) of the resin.

According to the results listed, the crosslink-
25 ing polyolefin type resin layer requires a thickness in a
proportion of 25% or more to the total thickness (sample
No. 2) and a gel fraction in a proportion of 20% or more
(sample No. 7). However, if the thickness is 40 μ or

1 more (sample No. 5), the proportion to the total thick-
ness exceeds 65%. The crosslinking polyolefin type resin
layer affects the other layer components, and thus soft
feeling was decreased because of the decrease of falling
5 bag resistance at low temperature. Further, if the
average gel fraction degree is 65% or more (sample No.
9), film forming ability by drwing is deteriorated.

The sample Nos. 3, 17 to 19 and 24 to 28 relate
to the resin component of the crosslinking polyolefin
10 type resin layer. By observing the results obtained from
these samples, it is understood that a polyolefin type
resin an ethylene- α -olefin copolymer resin and an EVA can
be used as an component of the crosslinking polyolefin
type resin layer. In the case of the ethylene- α -olefin
15 copolymer resin, all of the resins having a density of
0.894 and a crystalline melting point of 113°C (sample
No. 25) and having a density of 0.923 and a crystalline
melting point of 122°C (sample No. 28) exhibit good
physical properties, and thus it appears that the so-
20 called very-low density polyethylene, linear low density
polyethylene or low density polyethylene can be used. To
be noted herein is the performance of the sample No. 19.
As apparent from the sample No. 23, the PVDC and the
ethylene- α -olefin copolymer resin are less adhesive to
25 each other, and thus the film performance is decreased on
using them in an adjacent position to each other in a
laminated film. On the other hand, in the sample No. 19,
adhesive strength is improved by the irradiation of this

1 invention as described in Experimental Example 6.

The vinylidene chloride type resin layer is generally required for maintaining a level of gas barrier property in a thickness of at least 4 μ . However, the
5 thickness becomes 15 μ or more (sample No. 11), it becomes difficult to maintain falling bag resistance at low temperature.

The sample Nos. 3, 10, 17 and 20 - 22 relates to an appropriate thickness (upper limit) of the sealing
10 resin layer. It is generally considered that the sealing resin layer requires a thickness of at least 3 μ to serve as an oil resistant sealing layer. However, the upper limit is at most 40% (sample No. 21) of the total thickness. If it reaches 50% (ample No. 22), drawing ability
15 is deteriorated and heat shrinkability cannot be increased.





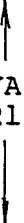




As for the resin components of the sealing resin layer, explanation is conducted in detail in Example, Comparative Example 2. By observing the sample
20 Nos. 3, 17 and 24 to 27, it is understood that the ethylene-olefin copolymer resin or the mixed resins containing said resin as a main component exhibit good physical property. This kind of film is generally used in a thickness of 40 μ (sample No. 15) to 80 μ (sample
25 No. 16). If it is thinner than the lower limit, it lacks durability as a package. If it is too thick, film forming ability by drawing is deteriorated and besides it lacks economy.

1 The sample Nos. 17 to 21, 23 to 27 are advantageously prepared economically by using three extruders. Among them, the sample Nos. 17, 18, 20 and 24 to 27 are considered to be a film having excellent performance and
5 high economy.

 As the result for the thickness construction, it is preferred that in the film of this invention in which the layer components are a crosslinking polyolefin type resin layer/a core layer/a adhesive shrinkable resin
10 layer/a sealing resin layer and the total thickness is in the range of 40 - 80 μ , the core layer has a thickness in the range of 4 μ or more and less than 15 μ , the sealing resin layer has a thickness of 4 μ or more but 40% or less of the total thickness, the crosslinking polyolefin
15 type resin layer having a gel fraction of 20 - 65% has a thickness in a proportion of 25% - 65% to the total thickness, and the balance with the adhesive shrinkable resin layer. Films having such a layer construction is excellent in film forming ability by drawing, heat
20 resistance and oil resistance and tough, and readily maintains heat shrinkability.

 The sample No. 28 is a film, in which on the outermost layer a resin having a higher crystalline melting point than the sealing resin layer and crosslink-
25 ing treatment was conducted so as to improve the heat resistance on the outermost layer.

Table 6-A

Sample No.	Layer construction of cylindrical film (thickness μ)					
	Exterior layer ← Interior layer					
	Outermost layer of crosslinking type resin layer I	Intermediate surface layer of crosslinking polyolefin type resin layer II	PVDC layer	Adhesive shrinkable resin layer	Sealing resin layer	
1	EVA1 (6)	EVA2 (4)		EVA2 (36)		
2	EVA1 (9)	EVA2 (6)		EVA2 (31)		
3	EVA1 (15)	EVA2 (10)		EVA2 (21)		Blend composition 1 (6)
4	EVA1 (21)	EVA2 (14)		EVA2 (11)		
5	EVA1 (24)	EVA2 (16)		EVA2 (6)		
6						
7						
8				EVA2 (10)		
9						
10				EVA1 (15)	EVA2 (12)	Blend composition 1 (15)
11			PVDC1 (15)	EVA2 (14)		
12			PVDC2 (8)	EVA2 (21)		
13			PVDC1 (8)	EEA (21)		
14			EVA3 (10)	PVDC1 (8)		EVA3 (21)
15	EVA1 (10)	EVA2 (6)	PVDC1 (4)	EVA2 (16)	Blend composition 1 (4)	
16	EVA1 (21)	EVA2 (14)	PVDC1 (10)	EVA2 (25)	Blend composition 1 (10)	

- Cont'd -

Table 6-A (Cont'd)

Gel frac- tion of crosslink- ing poly- olefin type resin layer (% by weight)	Evaluation result				
	Film forming ability by drawing	Heat shrink- ability	Retention rate of oxygen gas barrier pro- perty after rough treat- ment under se- vere condition	Oil resistance at high tem- perature	
				Exterior surface	dint
30	o	o	x	⊙	x
36	o	o	o	⊙	o
40	⊙	⊙	⊙	⊙	⊙
37	⊙	⊙	⊙	⊙	⊙
35	⊙	⊙	o	⊙	⊙
10	o	o	Δ	x	x
20	o	o	o	o	o
60	⊙	⊙	⊙	⊙	⊙
65	x	⊙	o	⊙	⊙
38	⊙	⊙	⊙	⊙	⊙
35	⊙	o	o	⊙	⊙
38	⊙	⊙	⊙	⊙	⊙
38	o	⊙	⊙	⊙	⊙
37	⊙	⊙	⊙	⊙	⊙
38	⊙	⊙	o	⊙	⊙
33	o	⊙	⊙	⊙	⊙

- Cont'd -

Table 6-A (Cont'd)

Falling bag re- sistance at low tempera- ture	Heat resist- ance of film
o	o
⊙	⊙
⊙	⊙
o	⊙
x	⊙
o	Δ
⊙	⊙
⊙	⊙
o	⊙
⊙	⊙
Δ	⊙
⊙	⊙
⊙	⊙
⊙	⊙
o	⊙
⊙	⊙

Note

EVA1: Vinyl acetate content, 10% by weight;

EVA2: Vinyl acetate content, 15% by weight;

EVA3: Vinyl acetate content, 20% by weight;

EEA: Ethylene-methyl acrylate copolymer resin, ethyl acrylate content, 7% by weight;






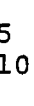

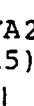




PVDC1: Vinylidene chloride-vinyl chloride copolymer resin, in which a comonomer component derived from the vinyl chloride monomer in the resin is in an amount of 17% by weight;

PVDC2: Vinylidene chloride-methyl acrylate copolymer resin, in which a comonomer component derived from the methyl acrylate monomer in the resin is in an amount of 10% by weight.

Blend composition 1:

Mixture of ethylene- α -olefin copolymer resin (density, 0.920; crystalline melting point, 120°C), trade name ULTZEX manufactured by MITSUI PETROCHEMICAL INDUSTRIES, LTD. /EVA2/ ethylene- α -olefin copolymer elastomer (density, 0.88; Vicat softening point, <40°C), trade name TAFMER manufactured by MITSUI POLYCHEMICAL CO. = 80/10/10

Table 6-B

Sample No.	Layer construction of cylindrical film (thickness μ)				
	Exterior layer \longleftrightarrow Interior layer				
	Outermost layer of crosslinking type resin layer I	Intermediate surface layer of crosslinking polyolefin type resin layer II	PVDC layer	Adhesive shrinkable resin layer	Sealing resin layer
17	A4 (10)	EVA2 (15)			
18	A4 (20)	EVA2 (5)			
19	A4 (25)	No layer			
20		EVA2 (15)			
21	A4 (10)	EVA2 (13)			
22		EVA2 (7)			
23		EVA2 (18)			
24	A5 (10)				
25	A6 (10)				
26	Blend composition 2 (10)	EVA2 (15)			
27	Blend composition 3 (10)				
28	A3 (10)				A5 (6)

- Cont'd -

Table 6-B (Cont'd)

Gel frac- tion of crosslink- ing poly- olefin type resin layer (% by weight)	Evaluation result				
	Film forming ability by drawing	Heat shrink- ability	Retention rate of oxygen gas arrier pro- perty after rough treat- ment under se- vere condition	Oil resistance at high tem- perature	
				Exterior surface	dint
38	⊙	⊙	⊙	⊙	⊙
37	⊙	⊙	⊙	⊙	⊙
35	⊙	⊙	○	⊙	⊙
40	⊙	⊙	⊙	⊙	⊙
39	○	○	⊙	⊙	⊙
38	x	Δ	⊙	⊙	⊙
40	Δ	○	x	⊙	⊙
36	⊙	⊙	⊙	⊙	⊙
39	⊙	⊙	⊙	⊙	⊙
38	⊙	⊙	⊙	⊙	⊙
40	⊙	⊙	⊙	⊙	⊙
39	⊙	⊙	⊙	⊙	⊙

- Cont'd -

Table 6-B (Cont'd)

		Note
Falling bag resistance at low temperature	Heat resistance of film	
		A1: Ethylene- α -olefin copolymer resin (density, 0.920; crystalline melting point, 120°C), trade name ULTZEX manufactured by MITSUI PETROCHEMICAL INDUSTRIES, LTD.
⊙	⊙	A3: Ethylene- α -olefin copolymer resin (density, 0.923; crystalline melting point, 122°C), trade name DOWLEX manufactured by DOW CHEMICAL CO.
⊙	⊙	A4: Ethylene- α -olefin copolymer resin (density, 0.906; crystalline melting point, 118°C), trade name NUCFLX manufactured by NIPPON UNICAR CO.
⊙	⊙	A5: Ethylene- α -olefin copolymer resin (density, 0.900; crystalline melting point, 115°C), trade name EXCELLENT VL manufactured by SUMITOMO CHEMICAL CO., LTD.
○	⊙	
Δ	⊙	A6: Ethylene- α -olefin copolymer resin (density, 0.894; crystalline melting point, 113°C), trade name NIPOLONL manufactured by TOYO SODA CO., LTD.
x ^{*1}	⊙	
⊙	⊙	Blend composition 1: Mixture of A4/A5 = 50/50;
⊙	⊙	Blend composition 2: Mixture of A4/A1 = 70/30;
⊙	⊙	EVA2: Vinyl acetate content, 15% by weight;
⊙	⊙	PVDC1: Vinylidene chloride-vinyl chloride copolymer resin, in which a comonomer component derived from the vinyl chloride monomer in the resin is in an amount of 17% by weight.
⊙	⊙	
		*1 In falling bag test, sealing parts in all bag samples were in ply separation between the PVDC layer and the inner layer.

1 Example, Comparative Example 2

For this invention, experiment was conducted in order to specifically explain the component and composition of the sealing resin layer which is as significant as the crosslinking polyolefin type resin layer.

That is, the basic construction of the film is designed as shown below using a film which was prepared from the sample Nos. 3, 17 and 24 to 28 used in Example, Comparative Example 1, and an apparatus illustrated in Fig. 5 in the same manner as in Example, Comparative Example 1. Samples comprising the resins listed in the item of "resin component of sealing resin layer" in Table 7-B as the component resin at the part of the sealing resin layer (sample Nos. 29 to 51) were used in experiment. The laminated films used in the experiment were 30 kinds in total.

Crosslinking polyolefin resin layer. (gel fraction, ca. 40%) 25 μ	EVA layer having a vinyl acetate content of 10%, 15 μ EVA layer having a vinyl acetate content of 15%, 10
PVDC layer (VDC : VC : = 87 : 13) 6 μ	
EVA layer having a vinyl acetate content of 15%, 23 μ	
Sealing resin layer 6 μ	

1 As for the 30 kinds of films, evaluation was
conducted referring to "reduction of defective rate of
sealing" and "reduction of time required for sealing"
which are the main objects of this invention, and
5 "transparency after shrinking" according to the methods
described herein. The results are listed in "results of
evaluation" in tables 7-A and 7-B.

The marks of "synthetic evaluation" in Tables
7-A and 7-B represent the grades using the following
10 criteria from the standpoint of the object (effect) of
this invention.

- ◎ : ◎ of all three items;
- : including the grade ○ referring to at least one
item (other may be in the grade ○ or ◎);
- 15 Δ : including the grade Δ referring to at least one
item (other may be in any grade);
- × : including the grade × referring to at least one
item (other must be in any grade)

In Table 7-A, most of the sealing resin layers
20 comprise an ethylene- α -olefin copolymer resin, and in
Table 7-B, most of the sealing resin layers comprise
mixed resins which contain an ethylene- α -olefin copolymer
resin as a main component.

Ethylene- α -olefin copolymer resins including
25 those having a density of 0.89 and a crystalline melting
point of 113°C (sample Nos. 24, 28) and a density of
0.923 and a crystalline melting point of 122°C (sample

1 No. 38) show excellent physical properties, so that it
appears that the so-called very-low density polyethylene,
linear low density polyethylene and low density
polyethylene can be used.

5 For the purpose of ready understanding of the
mixing ratio of an ethylene- α -olefin copolymer elastomer
and the EVA of the mixed resin in which the ethylene- α -
olefin copolymer resin is contained as a main component,
Fig. 7 is appended. This figure is an analytical diagram
10 of Table 7-A and 7-B, in which the marks of synthetic
evaluation are plotted on the positions of the components
of the sealing resin of the film. Fig. 7 illustrates by
spatial restriction only the parts which can be repre-
sented by the three components of the ethylene- α -olefin
15 copolymer resin, the ethylene- α -olefin copolymer
elastomer and the ethylene-vinyl acetate copolymer.

According to the results obtained from Fig. 7,
the composition of the sealing resin layer for satisfying
the aforementioned object of this invention is an
20 ethylene- α -olefin copolymer resin (resin A) having a
density of 0.93 and a crystalline melting point of 110 -
130°C, a mixed resin which comprises 60% by weight or
more of said resin A and 40% by weight or less of an
ethylene- α -olefin copolymer elastomer (resin B) or a
25 mixed resin which comprises 40% by weight or more of said
resin A, 5 -40% by weight of said resin B and 55% by
weight or less of an ethylene-vinyl acetate copolymer
resin (resin C), in which the total amount being 100%.

1 To be noted is sample No. 28, in which on the
outermost surface is arranged a resin having a crystal-
line melting point higher than that of the sealing resin
layer (the resin at the outermost layer of the crosslink-
5 ing polyolefin type resin layer: crystalline melting
point, 122°; the resin at the sealing resin layer:
crystalline melting point, 115°C), and the resin having a
higher crystalline melting point is crosslinked to
improve heat resistance. Accordingly, the sealing
10 performance is remarkably improved.

Table 7-A

Sample No.	Resin composition of sealing resin layer		Evaluation result			
	Resin used (Blending ratio, %)		Reject rate of sealing	Reduction required for sealing	Transparency after shrinking	Synthetic evaluation
3	A ₁ (80)	B ₁ (10)	C ₂ (10)	⊙	⊙	⊙
17	A ₄ (100)	-	-	⊙	⊙	⊙
24	A ₅ (100)	-	-	⊙	⊙	⊙
25	A ₆ (100)	-	-	⊙	⊙	⊙
26	A ₂ (50), A ₅ (50)	-	-	⊙	⊙	⊙
27	A ₂ (70), A ₁ (30)	-	-	⊙	⊙	⊙
28	A ₅ (100)	-	-	⊙ ^{*1}	⊙ ^{*2}	⊙

Note

- A1: Ethylene- α -olefin copolymer resin (density, 0.920; crystalline melting point, 120°C), trade name ULTZEX manufactured by MITSUI PETROCHEMICAL INDUSTRIES, LTD.
- A2: Ethylene- α -olefin copolymer resin (density, 0.920; crystalline melting point, 120°C), trade name ULTZEX manufactured by MITSUI PETROCHEMICAL INDUSTRIES, LTD.
- A3: Ethylene- α -olefin copolymer resin (density, 0.930; crystalline melting point, 122°C), trade name DOWLEX manufactured by DOW CHEMICAL CO.
- A4: Ethylene- α -olefin copolymer resin (density, 0.906; crystalline melting point, 118°C), trade name NUCFLX manufactured by NIPPON UNICAR CO.
- A5: Ethylene- α -olefin copolymer resin (density, 0.900; crystalline melting point, 115°C), trade name EXCELLENT VL manufactured by SUMITOMO CHEMICAL CO., LTD.

- Cont'd -

Table 7-A (Cont'd)

- A6: Ethylene- α -olefin copolymer resin (density, 0.894; crystalline melting point, 113°C), trace name NIPOLON L manufactured by TOYO SO'DA CO., LTD.
- B1: Ethylene- α -olefin copolymer elastomer (density, 0.88; VSP, 40°C or less;
- C2: EVA having a vinyl acetate content of 15% by weight.
- *1 Reject rate was zero.
- *2 Reject rate was zero even if cooling time was reduced to zero second.

1 Example, Comparative Example 3

As for 6 kinds of laminated films of the sample Nos. 17, 28, 29, 32, 33 and 34, evaluation was carried out referring to oil resistance of interior surface at 5 high temperature. The results are listed in Table 8.

According to the results listed in Table 8, it is understood that the film sample Nos. 17, 28, 29, and 32 to 34 are films of which interior surface is excellent in oil resistance at high temperature.

10 Therefore, this kind of the films is useful for packaging the processed meat such as receiving a fatty content in a cylindrical film and subjecting to sterilizing treatment at high temperature.

Table 8

Sample No.	Oil resistance of interior surface	(referential) Transparency after shrinking
17	◎	◎
28	◎	◎
29	◎	○
32	◎	◎
33	◎	◎
34	◎	◎

Table 7-B

Sample No.	Resin composition of sealing resin layer		Evaluation result			
	Resin used (Blending ratio, %)		Reject rate of sealing	Reduction required for sealing	Transparency after shrinking	Synthetic evaluation
29	A ₁	(100)	-	○	○	○
30	A ₂	(100)	-	◎	◎	◎
31	A ₄	(100)	-	◎	◎	◎
32	A ₁	(95)	-	○	◎	○
33	A ₂	(80)	-	◎	◎	◎
34	A ₁	(80)	C ₁ (10)	◎	◎	◎
35	A ₂	(80)	C ₁ (10)	◎	◎	◎
36	A ₁	(70)	C ₂ (25)	○	○	○
37	A ₁	(60)	-	◎	◎	○
38	A ₃	(60)	C ₂ (10)	◎	◎	◎
39	A ₁	(60)	C ₂ (20)	◎	◎	◎
40	A ₁	(50)	C ₂ (20)	◎	◎	◎
41	A ₃	(50)	C ₁ (40)	◎	◎	◎
42	A ₁	(40)	C ₂ (20)	◎	◎	○
43	A ₁	(40)	C ₂ (55)	◎	○	○
44	A ₁	(85)	C ₂ (15)	◎	x	x
45	A ₁	(60)	C ₂ (40)	○	x	x

- Cont'd -

Table 7-B (Cont'd)

46	A ₁ (50)	B ₁ (50)	-	x	○	○	x
47	A ₁ (40)	-	C ₁ (60)	Δ	○	○	x
48	A ₁ (30)	B ₁ (50)	C ₂ (20)	x	○	○	x
49	A ₁ (30)	B ₁ (20)	C ₂ (50)	x	⊙	○	x
50	D ₁ (100)	-	-	x	x	x	x
51	E ₁ (100)	-	-	x	x	x	x

Note

A1: Ethylene-α-olefin copolymer resin (density, 0.920; crystalline melting point, 120°C), trade name ULTZEX manufactured by MITSUI PETROCHEMICAL INDUSTRIES, LTD.

A2: Ethylene-α-olefin copolymer resin (density, 0.906; crystalline melting point, 118°C), trade name NUCFLX manufactured by NIPPON UNICAR CO.

A3: Ethylene-α-olefin copolymer resin (density, 0.923; crystalline melting point, 122°C), trade name DOWLEX manufactured by DOW CHEMICAL CO.

A4: Ethylene-α-olefin copolymer resin (density, 0.89; crystalline melting point, 116°C), trade name NUCFLX manufactured by NIPPON UNICAR CO.

B1: Ethylene-α-olefin copolymer elastomer (density, 0.88; VSP, 40°C or less;

C1: EVA having a vinyl acetate content of 10% by weight.

C2: EVA having a vinyl acetate content of 15% by weight.

D1: Ethylene-propylene copolymer resin having an ethylene content of 3.5 molar % (density, 0.90; crystalline melting point, 134°C).

E1: High density polyethylene (density, 0.953; crystalline melting point, 127°C).

1 Example, Comparative Example 4

As for the sample Nos. 17, 28, 36 to 43 and 45
to 49, evaluation as carried out referring to shrink-
ability at low temperature, oil resistance on interior
5 surface II and transparency of film according to the
methods described herein. The results are listed in
Table 9.

According to the results shown in Table 9, it
is understood that films in the groups of the sample Nos.
10 17, 28 and 36 to 42, particularly the sample Nos. 17, 28,
36, 38 to 42 are films excellent in shrinkability at low
temperature as well as other properties.

Accordingly, these films are those which are
useful for receiving a fatty content in a cylindrical
15 film, heat shrinking extensively the film at a low
temperature where the content will not be denaturated and
forming an attractive tight package of raw meat.

Table 9

Sample No.	Shrinkability at low temperature	Oil resistance on interior surface II	Transparency of film	(Referential) Transparency after shrinking
17	◎	◎	◎	◎
28	◎	◎	◎	◎
36	○	◎	○	○
37	◎	◎	△	◎
38	◎	◎	◎	◎
39	◎	◎	◎	◎
40	◎	◎	◎	◎
41	◎	◎	◎	◎
42	◎	○	○	◎
43	◎	△	△	○
45	◎	○	x	x
46	◎	○	x	○
47	◎	x	x	x
48	◎	x	△	○
49	◎	x	△	○

1 Example, Comparative Example 5

In the apparatus (method) illustrated in Fig. 5, three extruders were respectively arranged for the following resins:

5 for core layer (one extruder); PVDC (vinylidene chloride-vinyl chloride copolymer comprising a comonomer component derived from the vinyl chloride monomer in the resin in an amount of 7% by weight), for intermediate surface layer of the crosslinked polyolefin type resin
10 layer and adhesive shrinkable resin layer (one extruder); an ethylene-vinyl acetate copolymer resin having a vinyl acetate content of 15% by weight, the sealing resin and the outermost layer crosslinking resin layer (one extruder); [a mixed resin comprising an ethylen- α -olefin
15 copolymer resin having a density of 0.923 and a crystalline melting point of 122°C, (trade name, DOWLEX, manufactured by Dow Chemical Co.) in an amount of 80% by weight, an ethylene- α -olefin copolymer elastomer (trade name, TAFMER, manufactured by MITSUI POLYCHEMICAL CO.) in
20 an amount of 10% by weight and an ethylene-vinyl acetate copolymer resin having a vinyl acetate content of 15% by weight in an amount of 10% by weight. A cylindrical laminated film having a layer construction illustrated in the sample No. 52 in Table 10 and a gel fraction of 36%
25 by weight was accomplished.

In the same time, commercially available films G (manufactured by G Co.) and K (manufactured by K Co.) were obtained, of which layer construction is listed in

1 Table 10. These samples were evaluated together with the
representative film sample Nos. 17, 28, 34 and 39 of this
invention prepared in Example, Comparative Examples 1 and
2 with reference to substantially all of the evaluation
5 methods described herein to examine synthetically the
film properties of this invention in the field of
application. The results are listed in Table 1.

According to the result listed in Table 11, it
can be appreciated that the films of this invention are
10 superior to commercially available films in all evaluation items and particularly excellent in heat sealability which is useful for improving the packaging efficiency.

For the application which requires high
15 temperature oil resistance there can be used the films of the sample Nos. 34 and 52, and for the application which requires heat shrinkability at lower temperature at high level, there can be selected the film of the sample No. 39. Further, the films of the sample Nos. 17 and 28 have
20 both said heat shrinkability and high temperature oil resistance, so that they are convenient films which can be used for packaging either raw meat or processed meat. Thus, the film performance of this invention can be appreciated more prominent.

25 Moreover, according to this invention, a film having a five-layer structure and excellent properties can be advantageously prepared by using three extruders with an appropriate selection of layer construction.

Table 10

Sample No.	Layer construction of cylindrical film Exterior layer \longleftrightarrow Interior layer
17	<p>Crosslinking*1</p> <p>$\overbrace{A_4/EVA(Vac. 15\%)/PVDC_1/EVA(Vac. 15\%)/A_4}$</p> <p>10 μ / 15 μ / 8 μ / 21 μ / 6 μ</p>
28	<p>Crosslinking*2</p> <p>$\overbrace{A_3/EVA(Vac. 15\%)/PVDC_1/EVA(Vac. 15\%)/A_5}$</p> <p>10 μ / 15 μ / 8 μ / 21 μ / 6 μ</p>
39	<p>Crosslinking*3</p> <p>$\overbrace{EVA(Vac. 10\%)/EVA(Vac. 15\%)/PVDC_1/EVA(Vac. 15\%)/Blend\ compo-}$ sitition 2</p> <p>15 μ / 10 μ / 6 μ / 23 μ / 6 μ</p>
34	<p>Crosslinking*4</p> <p>$\overbrace{EVA(Vac. 10\%)/EVA(Vac. 15\%)/PVDC_1/EVA(Vac. 15\%)/Blend\ compo-}$ sitition 3</p> <p>15 μ / 10 μ / 6 μ / 23 μ / 6 μ</p>
52	<p>Crosslinking*5</p> <p>$\overbrace{Blend\ compo- / EVA(Vac. 15\%)/PVDC_1/EVA(Vac. 15\%)/Blend\ compo-}$ sitition 4</p>

- Cont'd -

Table 10 (Cont'd)

Gel fraction of crosslinkg poly- olefin resin layer (% by weight)			Gradient of gel fraction [y/x]
Whole layer	Outermost layer [x]	Surface layer in layer (I) side [y]	
38 (part of *1)	47	12	0.25
39 (part of *2)	46	13	0.28
37 (part of *3)	-	-	-
39 (part of *4)	-	-	-
36 (part of *5)	-	-	-

- Cont'd -

Table 10 (Cont'd)

Commer- tially avail- able film G	Crosslinking*6 EVA (Vac. 10%) / PVDC / EVA (Vac. 10%)		
	15 μ	10 μ	35 μ
Commer- tially avail- able film K	EVA (Vac. 10%) / EVA (Vac. 15%) / PVDC / EVA (Vac. 15%) / IONOMER		
	15 μ	2 μ	8 μ / 2 μ / 34 μ

- Cont'd -

Table 10 (Cont'd)

41 (part of *6)	-	-	-	-
	-	-	-	-

Table 11

Sample No.	Heat shrink-ability at low temperature	Shrink-ability	Barrier properties		Falling bag resistance at low temperature	Heat resistance of films	Reject rate of sealing	Reduction of time required for sealing
			After rough treatment under severe condition	After flexing with twisting				
17	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙
28	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙
39	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙
34	○	⊙	⊙	⊙	⊙	⊙	⊙	⊙
52	Δ	⊙	⊙	⊙	⊙	⊙	⊙	⊙
Com. avail. pro. G	x	⊙	x	⊙	○	⊙	Δ	Δ
Com. avail. pro. K	x	⊙	Δ	x	x	x	x	x

- Cont'd -

Table 11 (Cont'd)

Oil resistance on exterior surface	Oil resistance on dint	Oil resistance on interior surface	Oil resistance on interior surface II	Trans- parency of film	Trans- parency after shrinking	Trans- mission of oxygen gas *1
⊙	⊙	⊙	⊙	⊙	⊙	21
⊙	⊙	⊙	⊙	⊙	⊙	20
⊙	⊙	Δ	⊙	⊙	⊙	27
⊙	⊙	⊙	⊙	⊙	⊙	26
⊙	⊙	⊙	⊙	⊙	⊙	27
x	⊙	Δ	⊙	⊙	⊙	35
x	x	Δ	o	⊙	Δ	17

*1: Measured in accordance with ASTM D 3985;
unit; cc/m².24 hrs.atm. (at 23°C)

1 INDUSTRIAL APPLICABILITY

As explained above, this invention accomplished for the first time a co-extruded cylindrical laminated film having a surface crosslinking resin layer which was
5 irradiated with electron rays. This crosslinking resin layer improves film forming ability by drawing during the production process and also improves as a resin layer the heat resistance, oil resistance, rub resistance, toughness and the like, to improve the whole properties of the
10 film. In addition, the crosslinking resin layer leads to the firm bonding with the core layer. Particularly, in the film of this invention there are arranged a heat resistant crosslinking resin invention there are arranged a heat resistant crosslinking resin and a sealing resin
15 layer of a selected resin at the surface layer and the innermost layer, respectively, so that as a combination effect thereof great effect is exhibited for the reduction of the sealing time which serves for improving the packaging ability and the elimination of defective rate
20 at sealing part. This effect leads to settlement of the most serious problem in the art of packaging, and thus this invention is very useful to industry.

CLAIMS

1. A heat shrinkable cylindrical laminated film having a polyvinylidene chloride type resin (I) as an oxygen gas barrier core layer on the both surface sides of which 1 or 2 resin layers are arranged respectively and consisting of 3 - 5 layers with total, characterized in that the cylindrical exterior surface resin layer on said layer (I) comprises a crosslinked polyolefin type resin layer (II) having a gel fraction [x] at the outermost layer of 25 - 70% by weight, a gel fraction [y] at the surface layer in the side of the layer (I) of 40% by weight or less and a gradient of gel fraction represented by $[y/x]$ of 0.6 or less and the joint of said layers (I) and (II) comprises a laminate of a joint in a state denaturated by electron rays.
2. A laminated film according to Claim 1, wherein the average gel fraction of the crosslinked polyolefin type resin layer (II) is in a range of 20 - 60% by weight and the thickness of the layer is in a proportion of 25 - 65% to the total thickness of the film.
3. A laminated film according to any one of Claims 1 or 2, wherein the crosslinked polyolefin type resin layer (II) comprises two resin layers, the crosslinking efficiencies of which are different from each other, and has a two layer structure in which one of the resin layers having a lower crosslinking efficiency is arranged as an outermost layer.
4. A laminated film according to Claim 1, wherein

a sealing resin layer (IV) is arranged through the adhesive shrinkable resin layer (III) in the interior surface side of said layer (I) of the cylinder.

5. A laminated film according to Claim 4, wherein said adhesive shrinkable resin layer (III) is an ethylene-vinyl acetate copolymer resin having a vinyl acetate content in the range of 13 - 20% by weight.

6. A laminated film according to Claim 4, wherein said sealing resin layer (IV) is any one of the resin layers of an ethylene- α -olefin copolymer resin (resin A) having a density of 0.88 - 0.93 and a crystalline melting point of 110 - 130°C, a mixed resin comprising 60% by weight or more of said resin A and 40% by weight or less of an ethylene- α -olefin copolymer elastomer (resin B) or a mixed resin comprising 40% by weight or more of said resin A, 5 - 40% by weight of said resin B and 55% by weight or less of an ethylene-vinyl acetate copolymer resin (resin C), in which the percentages of the components in said mixed resins amount to 100% in total.

7. A laminated film according to Claim 1, wherein said crosslinked polyolefin type resin layer (II) comprises any one of an ethylene- α -olefin copolymer resin (resin A) having a density of 0.88 - 0.93 and a crystalline melting point of 110 - 130°C or an ethylene-vinyl acetate copolymer resin (resin D), and the construction thereof is a single layer of the resin A or the resin D, a double layer combined with the resin D, or a combination

of two layers in which the outermost surface layer consists of the resin A and the inner surface layer consists of the resin D.

8. A laminated film according to Claim 1, wherein said polyvinylidene chloride type resin layer (I) is a vinylidene chloride-vinyl chloride copolymer resin having a content of the vinyl chloride component as a comonomer of 10 - 25% by weight.

9. A laminated film according to Claim 1, wherein said polyvinylidene chloride type resin layer (I) is a vinylidene chloride-methyl acrylate copolymer resin having a content of the methyl acrylate component as a comonomer of 3 - 15% by weight.

10. A laminated film according to Claim 4, wherein in both of the crosslinked polyolefin type resin layer (II) and the sealing resin layer (IV), the same resin selected from the resins of the sealing resin layer is arranged.

11. A laminated film according to Claim 4, wherein in both of inner surface layer of the crosslinked polyolefin type resin layer (II) and the adhesive shrinkable resin layer (III), an ethylene-vinyl acetate copolymer resin is arranged.

12. A laminated film according to Claim 4, wherein the laminated film has a thickness of 40 - 80 μ in total, the core layer (I) having a thickness of 4 - 15 μ , the adhesive resin layer (IV) having a thickness of 4 μ or more and 40% or less in proportion to the total

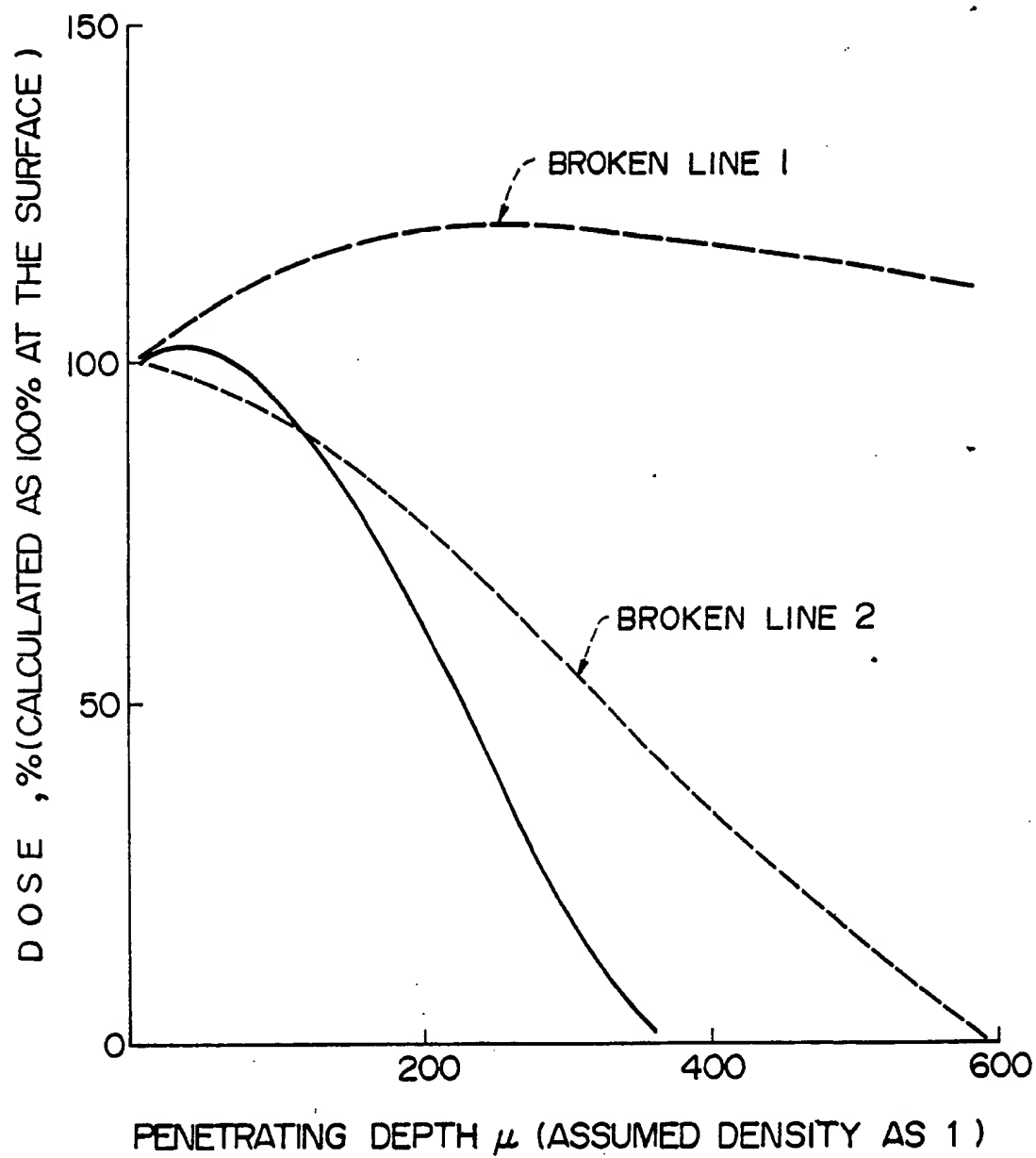
thickness, the crosslinked polyolefin type resin layer (II) having a thickness of 25 - 65% in proportion to the total thickness and the sealing shrinkable resin layer (III) having a thickness of balance.

13. A laminated film according to Claim 4, wherein the laminated film is used for heat shrinkable packaging of the content of a fatty irregularly shaped food.

14. A laminated film according to any one of Claims 1 or 4, wherein the laminated film is a co-extruded and seamless cylindrical film.

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FIG. 1



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FIG. 2

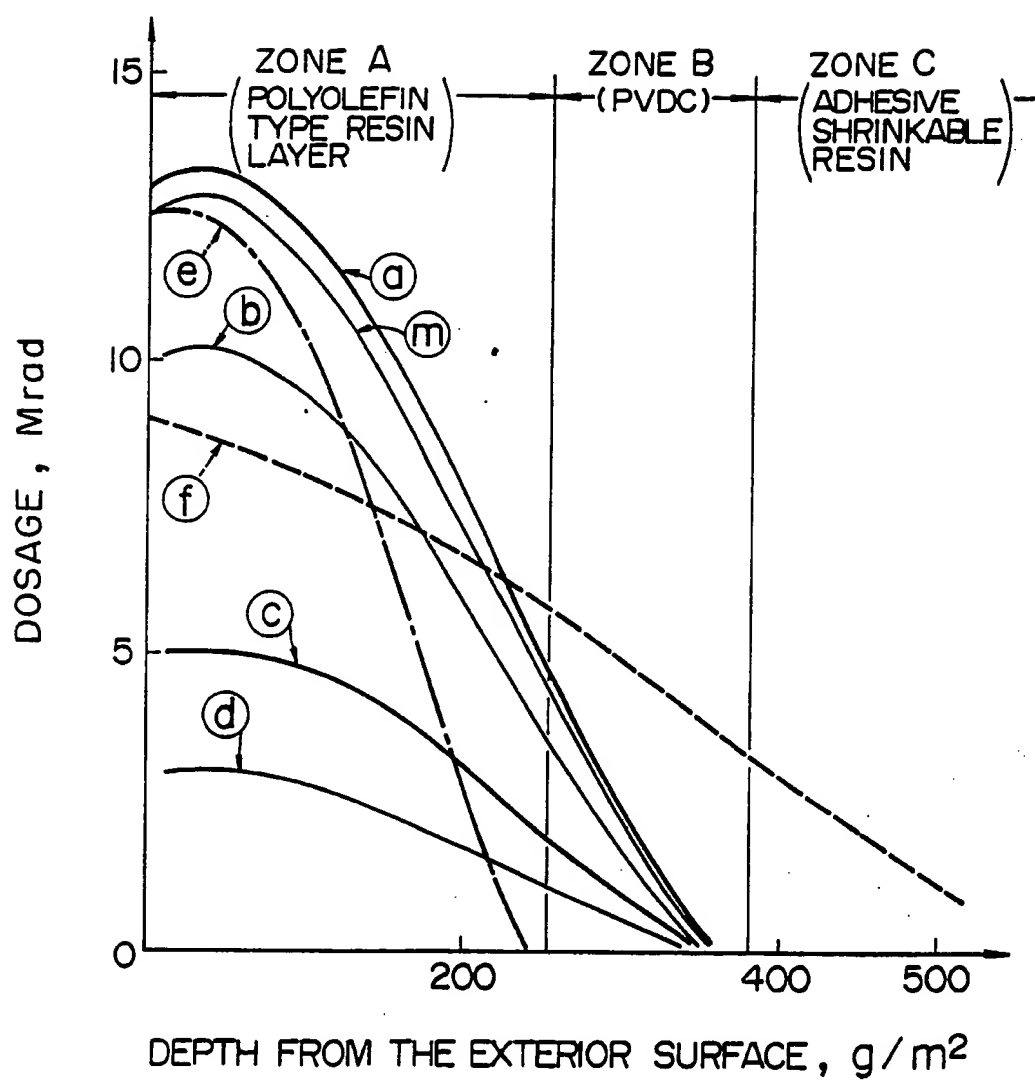


FIG. 3A 3/8

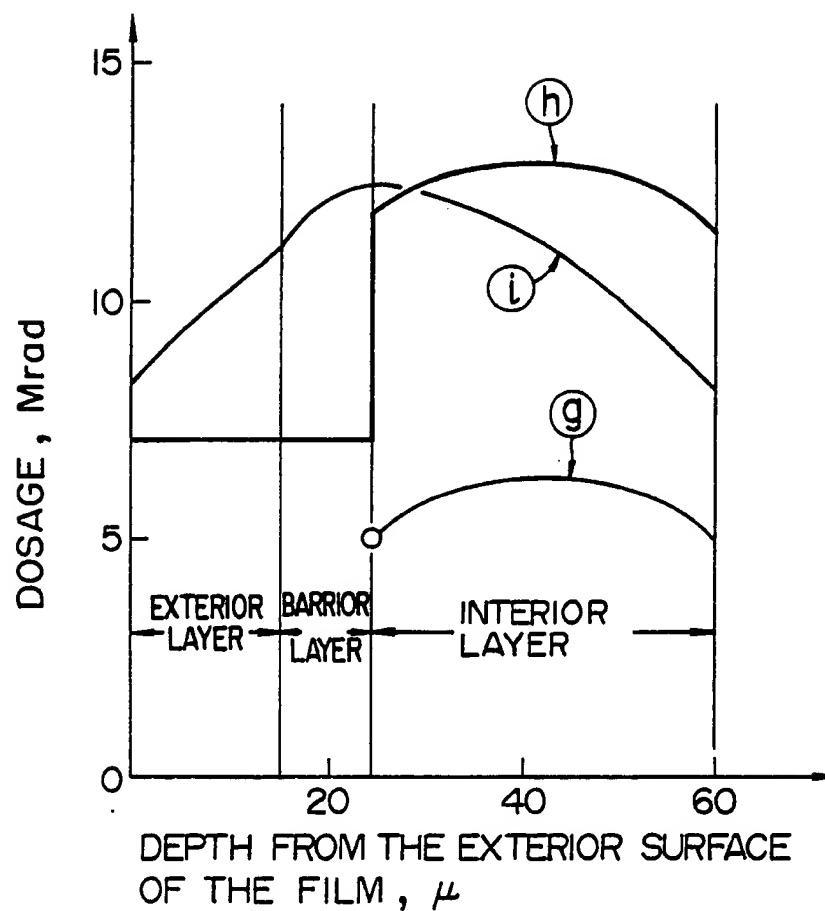
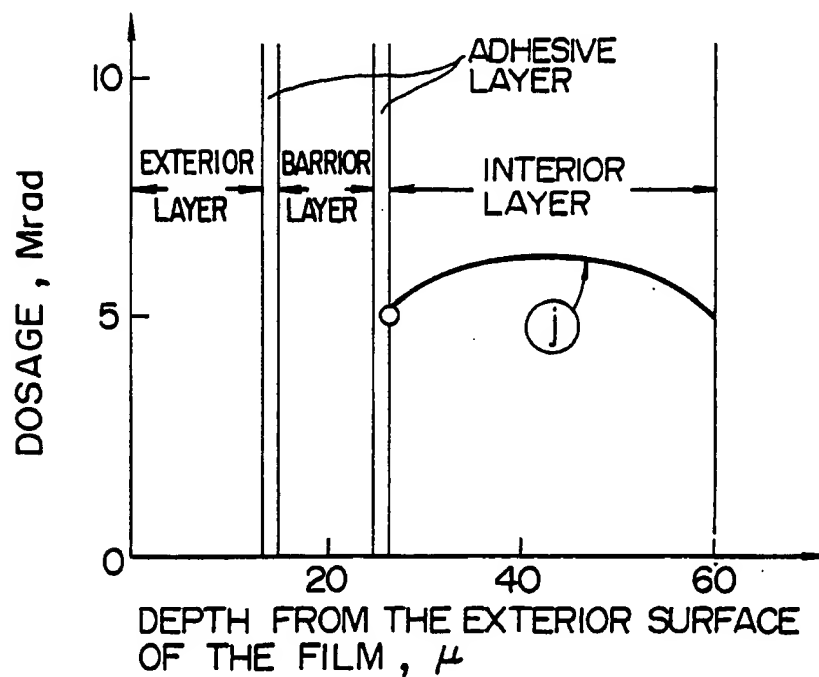


FIG. 3B



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FIG. 4

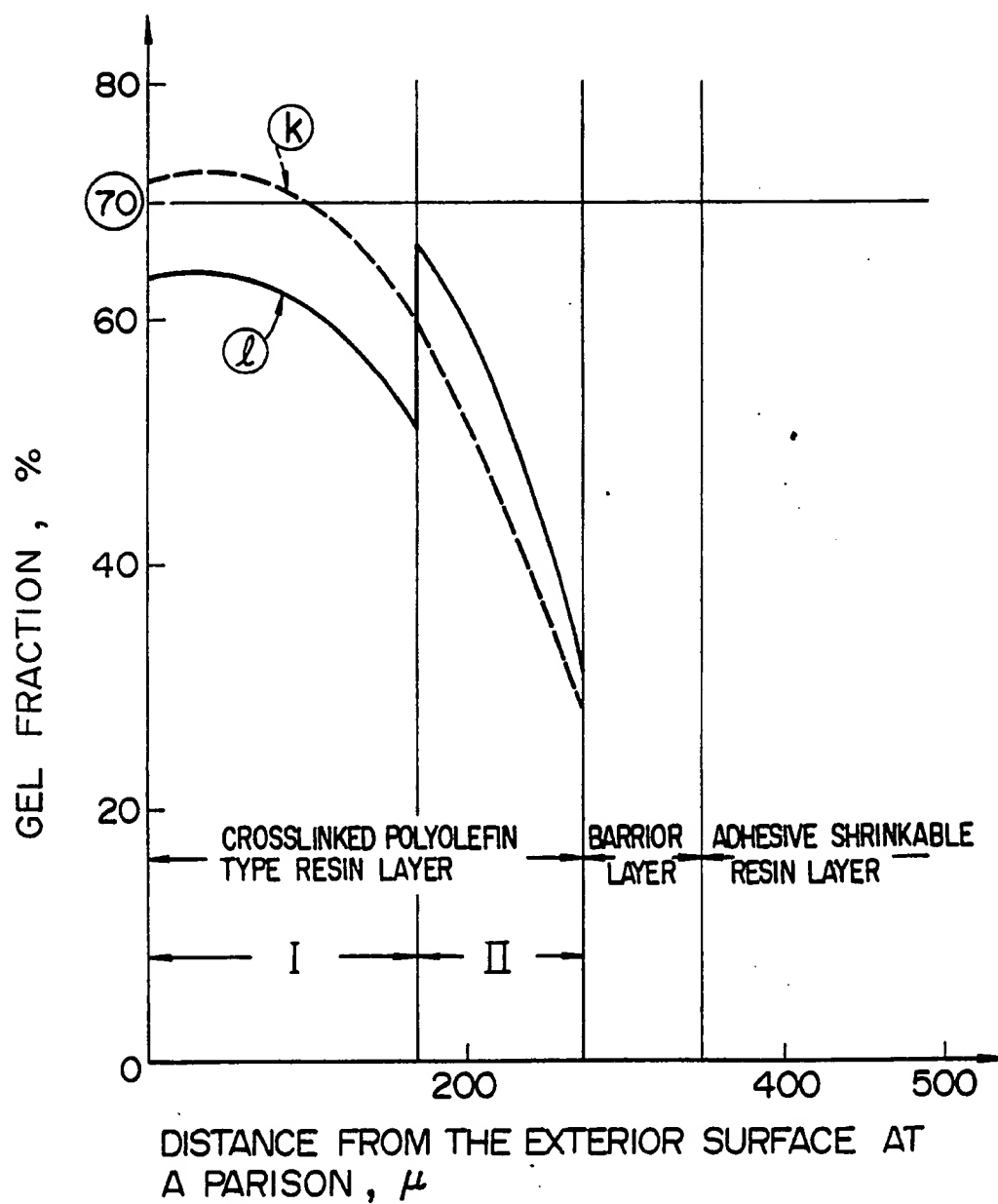
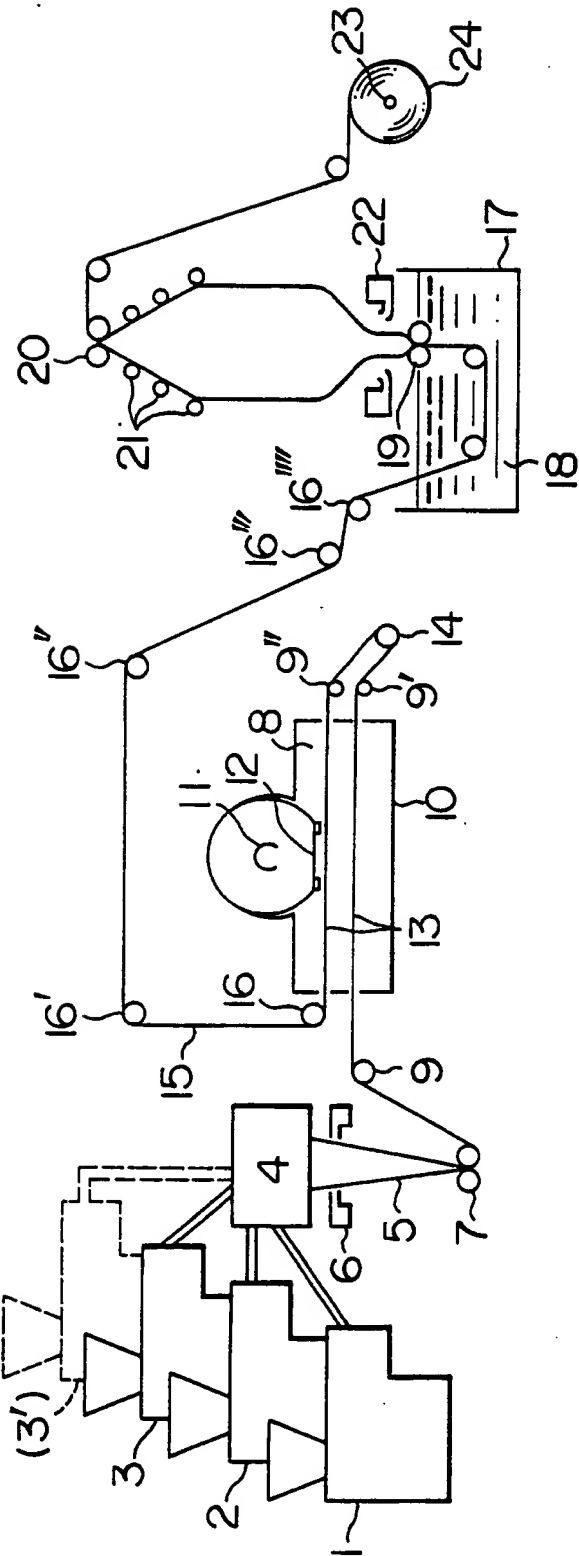


FIG. 5



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FIG. 6

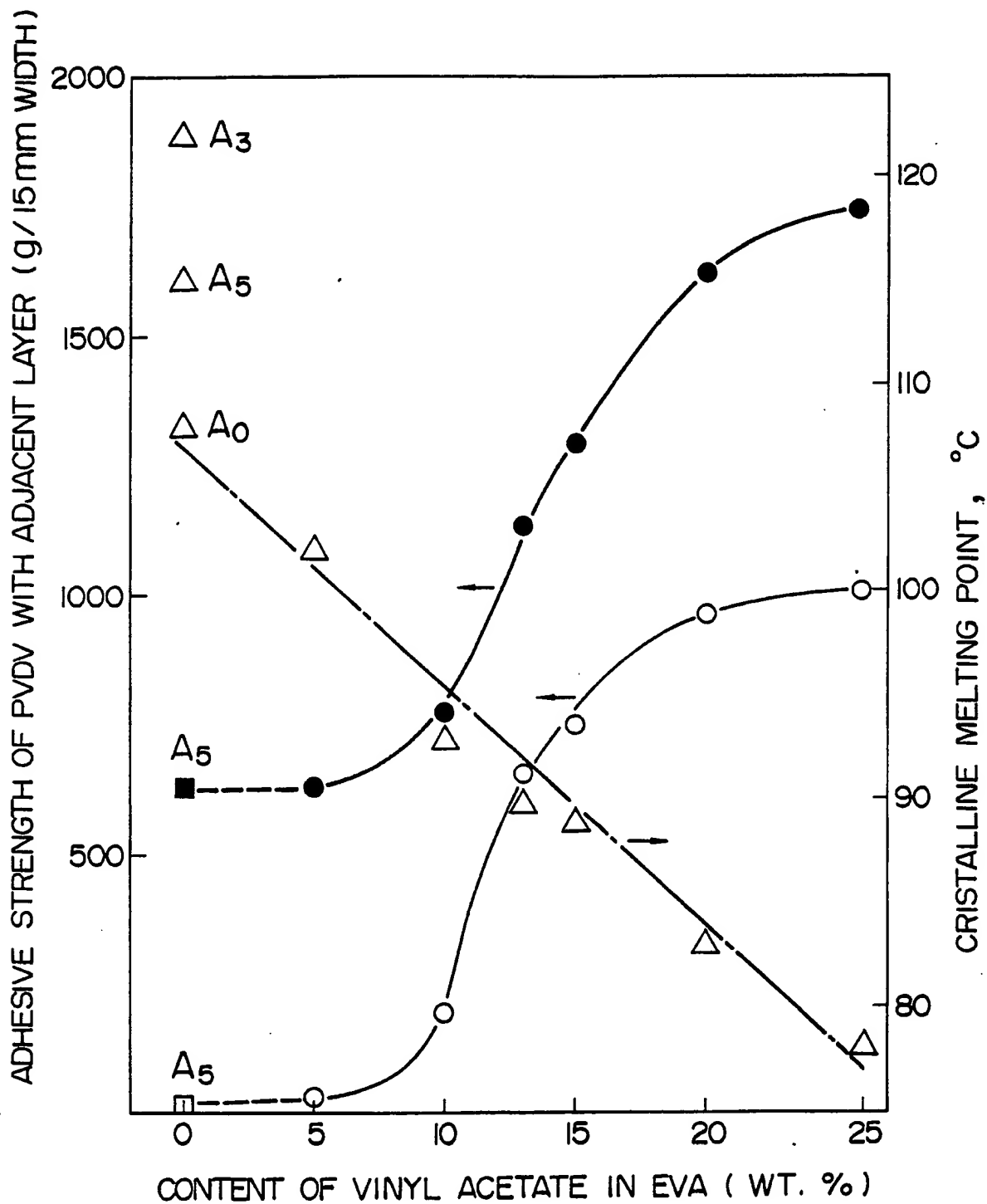


FIG. 7

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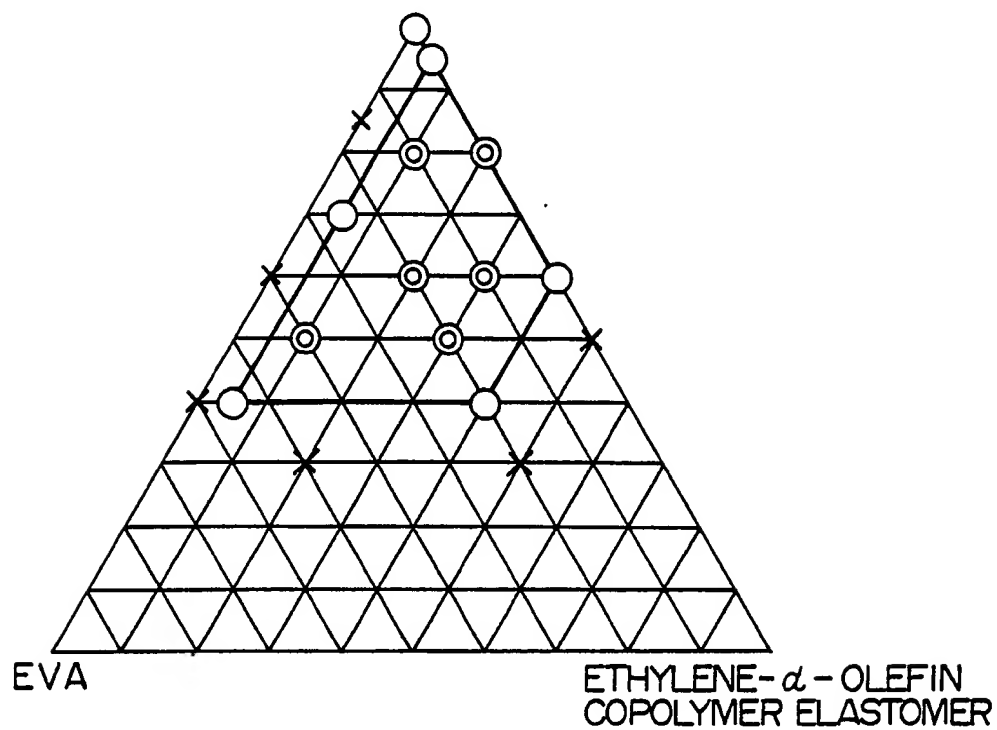
ETHYLENE- α -OLEFIN COPOLYMER RESIN

FIG. 8

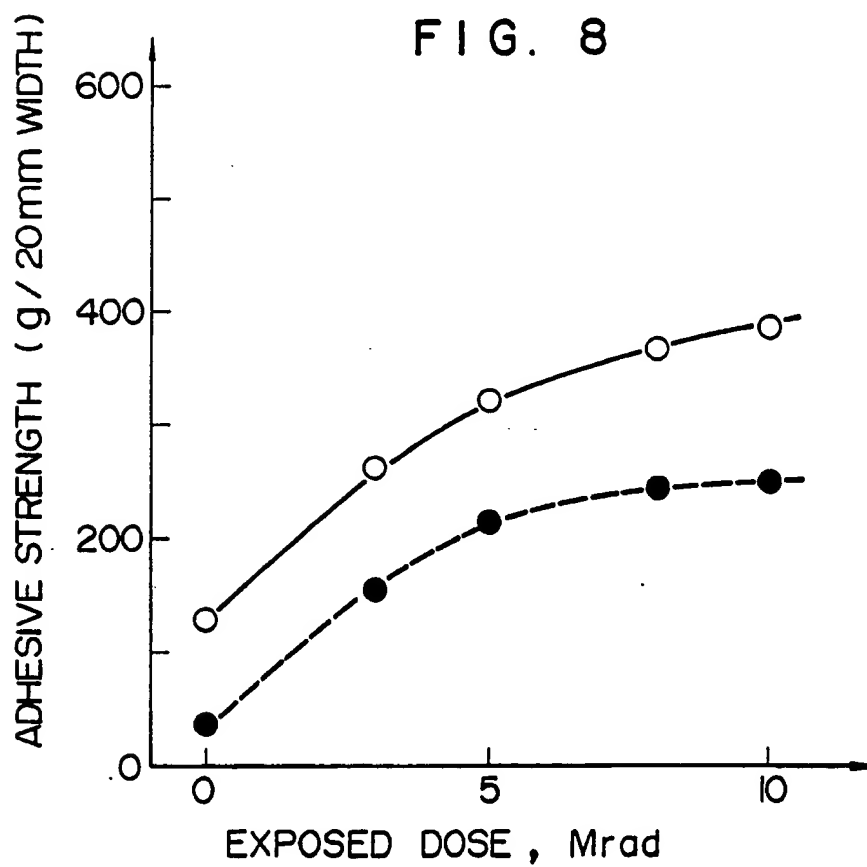
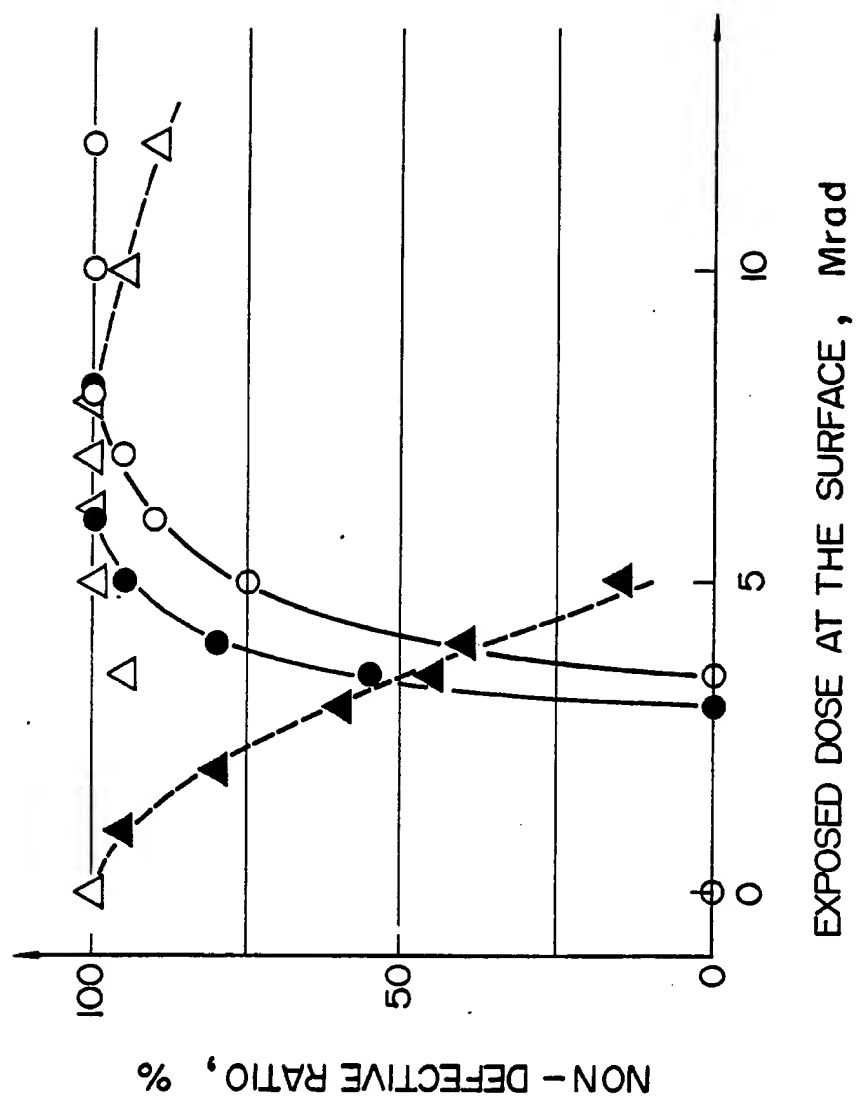


FIG. 9



INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 87/00401

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : B 65 D 65/40; B 32 B 27/30; B 32 B 31/28		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC ⁴	B 32 B	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP, A, 0022184 (BAYER AG) 14 January 1981 see claim 1 -----	1
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the international Search		Date of Mailing of this International Search Report
21st September 1987		15 OCT 1987
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		M. VAN MOL

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/JP 87/00401 (SA 17603)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/09/87

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0022184	14/01/81	DE-A- 2925205	05/02/81
		JP-A- 56005834	21/01/81
		AU-A- 5913680	08/01/81
		CA-A- 1141700	22/02/83

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